

NITROGEN AND PHOSPHORUS CYCLING IN MIDWESTERN
AGRICULTURAL WETLANDS IN RESPONSE TO ALTERED
HYDROLOGIC REGIMES

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ABSTRACT

Allyson Shaidnagle Smith

NITROGEN AND PHOSPHORUS CYCLING IN MIDWESTERN AGRICULTURAL WETLANDS IN RESPONSE TO ALTERED HYDROLOGIC REGIMES

The transfer of nutrients from US Midwest croplands into surface waters causes eutrophication and a decline in water quality. Temporary retention of nutrient-rich runoff in constructed wetlands can help mitigate these negative impacts through physical entrapment and biological transformation of nitrogen (N) and phosphorus (P). However, with the expectation that wet-dry periods will be more frequent in the region, there is a need to better understand the mechanisms that control nutrient retention and release in US Midwest wetlands constructed on former croplands. In this study, soil cores (30 cm long, 20 cm diam) were collected from two constructed wetlands (4 and 8-yr old), and the surface (0-20 cm) and subsurface (40-60 cm) layers of a cropland where a constructed wetland will be constructed in the future. Soil cores were subjected to either a moist or a dry treatment for 5 weeks, and then flooded with stream water (water depth 6 cm). The flux of nutrients, N_2O , cations, and variation in floodwater chemistry (pH and ORP) were monitored for another 5 week period. Porewater was tested during the final 3 weeks of the experiment. Nitrate ($0.1\text{-}130 \text{ mg N m}^{-2} \text{ d}^{-1}$) and inorganic P (P_i) fluxes ($0.09\text{-}2.9 \text{ mg P m}^{-2} \text{ d}^{-1}$) were significantly higher in the dry treatment cores. Regardless of site, the dry treatment also resulted in higher floodwater NO_3^- concentrations suggesting organic matter mineralization and mineral N build up during the drying phase. However, this

initial NO_3^- release was rapidly denitrified as indicated by the sharp increase in N_2O production during that period. In contrast to N, the release of P_i was significantly higher in cores from the cropland. Soil at these sites had higher water extractable P_i and total P. Contrary to the study hypothesis and the results of previous studies, P_i concentration in floodwater and porewater was not correlated with dissolved Fe suggesting that reductive dissolution was not the dominant process controlling P release in US Midwest mineral soils developed from calcareous glacial till. Rather, variation in Ca^{2+} concentration and its relationship with P_i suggest that dissolution of Ca-containing minerals may be more important and should be the focus of future studies examining the geochemistry of P in these constructed wetlands.

Pierre-Andre Jacinthe, Ph.D., Committee Chair

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LIST OF ABBREVIATIONS

TP	Total Phosphorus
SRP	Soluble Reactive Phosphorus
TDP	Total Dissolved Phosphorus
DOP	Dissolved Organic Phosphorus
DOC	Dissolved Organic Carbon
TC	Total Carbon
TN	Total Nitrogen
NO_3^-	Nitrate
NH_4^+	Ammonium
SB-1	Schoolbranch Site #1
SB-2	Schoolbranch Site #2
W-1	Wetland Site #1
W-2	Wetland Site #2

INTRODUCTION

Statement of Problem

Intensive agricultural practices over the past 100 years have resulted in soil-nutrient enrichment, excessive nutrient loadings from land to surface waters, deterioration of drinking water quality, and a host of other problems in aquatic ecosystems. Nitrogen (N) and phosphorus (P) are the primary nonpoint pollutants of concern in agricultural watersheds (Kovacic et al., 2000). Sustained nutrient input into surface waters results in eutrophication, a condition which can negatively impact water quality across a range of aquatic ecosystems including streams, lakes, reservoirs and coastal areas (USGS, 1999). When other conditions (e.g. light and temperature) are optimal, these nutrient-enriched aquatic ecosystems often experience algal blooms. Decomposition of algal biomass by resident microbes leads to dissolved oxygen (DO) depletion, ultimately resulting in hypoxia and enhanced potential for fish kills (Carpenter et al., 1998). Evidence of eutrophication has been documented in many coastal areas of the United States due to enhanced monitoring activities by the National Oceanic and Atmospheric Administration's (NOAA) National Estuarine Eutrophication Assessment. In a 1999 NOAA report, 44 of the 139 monitoring sites showed elevated signs of eutrophic conditions, with an additional 36 sites showing intermediate signs of eutrophication (Bricker et al., 1999). The Gulf of Mexico is one of the best-known and also one of the largest coastal areas in the US affected seasonally by eutrophication (Howarth, 2002). The size of the so-called "dead zone" (dissolved oxygen levels $< 2 \text{ mg L}^{-1}$) in the Gulf has grown from 7,700-9,000 km^2 prior to 1993 to 15,000-20,000 km^2 in 2006 (Joyce, 2000; Mitsch and Gosselink, 2007). With 58% of the Mississippi River basin under

various agricultural land-uses (NRC, 2008), available information indicates that agriculture intensification has the greatest impact on water quality and ecosystem health in the Mississippi River delta (Turner and Rabalais, 2003). Analysis of sediment cores collected at the mouth of the Mississippi River has shown increased levels of biogenic silica in diatom remains (indicating increased primary productivity), and this trend was found to correlate with increased N fertilizer use over the past 50 years in the Mississippi Basin (Turner and Rabalais, 2003). Since diatom growth is generally N-limited, increased availability of this nutrient may have allowed diatom populations to proliferate.

In response to increasing concerns on the health of aquatic ecosystems, treatment wetlands have been proposed as a possible solution to help reduce the export of nutrients from croplands and thus improve water quality. Treatment wetlands are defined as natural, surface and subsurface constructed wetlands whose sole purpose is to treat polluted waters (Mitsch and Gosselink, 2007). In addition to providing a low-cost alternative for wastewater processing, wetlands have a number of applications including the treatment of tertiary municipal wastewater, acid mine drainage, and urban and agricultural runoff (Mungasavalli and Viraghavan, 2006; Verehoeven et al., 2006). There is a growing body of published literature describing individual case studies of treatment wetland effectiveness for point and nonpoint source pollutants. Treatment wetlands have been evaluated for their capacity to reduce the export of estrogens from animal feeding facilities (Shappell et al., 2007) and the export of heavy metals from coal-ash processing plants (Ye et al., 2001). These studies (Shappell et al., 2007; Ye et al., 2001) illustrate the efficiency of constructed wetlands in the control of pollutants originating from point sources. However, the control of diffuse pollutants has been more challenging because of

the multiplicity of sources (overland, atmospheric and subsurface) and seasonal variability of inputs (Carpenter et al., 1998). Although nonpoint source (NPS) pollution is harder to control, case studies have shown that natural and created wetlands have been effective in retaining stream sediment during flood events (Mitsch and Gosselink, 2007), metals from urban storm water runoff (Mungasavalli and Viraghavan, 2006) and nutrients from agricultural areas (Koskiaho and Puustinen, 2005; Verehoeven et al., 2006).

While various reports documenting the effectiveness of treatment wetlands in controlling point and NPS pollution have been published, much of the focus has centered on nutrients. Nitrogen and phosphorus retention studies in wetlands treating municipal wastewater, confined animal operations, and storm water runoff have resulted in significant nutrient reductions. After two years of monitoring nutrient loads in a municipal wastewater treatment wetland in Western Ireland, Healey and Cawley (2002) reported an average reduction of total N (TN) and total P (TP) of 51% and 13%, respectively. Furthermore, after 13 years of operation, the Houghton Lake, MI wastewater polishing wetland has maintained very high N and P retention, with DIN (dissolved inorganic N) and TP retention values ranging from 82-99% and 94-99%, respectively (USEPA, 1993). Similar to municipal wastewater systems, treatment wetlands designed to purify livestock wastewater have also shown effective nutrient processing potential. Hunt et al. (1995) reviewed the nutrient retention effectiveness of 7 US swine and dairy farm treatment wetlands, and reported TP and $\text{NH}_4\text{-N}$ (ammonium-N) reductions between 59-80% and 54-94%, respectively. Knight (2000) reported a slightly lower rate of TP and TN reduction (42% on average) from a review of nutrient removal from 135 animal wastewater wetlands across the US. Human and animal

wastewater nutrient retention on average is less variable than storm-water runoff mostly due to flow variability. Mungasavalli and Viraghavan (2006) reviewed 12 storm water treatment wetlands throughout the world and reported a wide range of removal efficiencies for TN and TP, 11-75% and 17-90%, respectively. Casey and Klaine (2001) monitored nutrient retention in a riparian wetland receiving runoff from fertilized golf courses in South Carolina. After studying 11 sequential flow events, NO_3^- and PO_4^{3-} removal averaged 80 and 74%, respectively, supporting the hypothesis that wetlands can effectively remove large amounts of N and P under variable flow conditions.

Specifically placed within agricultural landscapes, treatment wetlands can trap and transform excess nutrients, improving downstream water quality (Mungasavalli and Viraghavan, 2006). Wetlands are valuable nutrient processing systems due to the complex and highly active microbial communities that they support. However, treatment wetland effectiveness is highly variable, and past studies have associated this variability to hydrologic regime, water residence time, and wetland to catchment area ratios. Jordan et al. (2003) conducted a 2-year study at a restored wetland receiving cropland runoff in Maryland and reported an average reduction of 52% NO_3^- , 25% NH_4^+ and 27% TP during the study period. These authors also noted that, during the second year of monitoring, N and P retention was significantly lower and ascribed the wetland limited performance due to the highly variable and unsteady flow conditions. They (Jordan et al., 2003) further concluded that the nutrient attenuation capacity of the wetland can be improved under steady and slow flow rates allowing for optimal biogeochemical transformations of nutrients entering the wetland. The hydraulic residence time of a wetland (time needed

for processing incoming nutrients) is a function of the nutrient load, wetland size and hydrologic regime (Mungasavalli and Viraghavan, 2006).

The question of increased water residence time is particularly relevant to Midwestern wetlands since the majority of the nutrient runoff typically occurs during only a few, very intense rainfall events. Royer et al. (2006) reviewed 10 years of N and P export in three watersheds in Illinois to find that 56% of the NO_3^- and 84% of the dissolved reactive phosphorus (SRP) runoff occurred during only 10% of the time (>90 percentile storm events). In other words, storms producing the highest flows carried the largest nutrient flux from agricultural fields to nearby streams, occurring seasonally from mid January to June (Royer et al., 2006). Typically, the largest rainfall events occur in the winter and spring; thus, the bulk of nutrients are exported from agricultural areas during these periods (Gentry et al., 1998; Tomer et al., 2003). As a result, nutrient levels in Midwestern streams tend to decrease significantly ($<2 \text{ mg N L}^{-1}$) in late summer and early fall (Gentry et al., 1998). Since the largest rainfall events in the Midwest normally occur during winter and spring, wetlands have to be large enough to process incoming nutrient loads during these periods.

In the Midwest, nutrient export from agricultural fields occurs via surface (overland) flow and subsurface tile drains. In poorly drained agricultural soils of the Midwest, subsurface tile drains are used to keep soils from becoming saturated for extended periods of time. Subsurface tiles have been used to drain cropland since early European settlement. Tiles are usually 20-50 cm diameter pipes typically placed 1-1.5 m below the surface providing a quick conduit for water drainage. Intricate systems of these pipes connect together under fields eventually terminating at the closest drainage

ditch or stream. Due to this delivery mechanism, tile drains have the capacity to carry high nutrient loads to streams (Gentry et al., 1998; Tomer et al., 2003). After a 9 year tile drain NO_3^- flux study in Central Iowa, outlet concentrations exceeded the USEPA maximum contaminant level of 10 mg N L^{-1} during 70-80% of the study period. The results of this study also showed that although large storms (intensity 0.1 mm h^{-1}) occurred only 6-10% of the time, they contributed to the highest NO_3^- fluxes recorded, accounting for up to 74% of the total N load (Tomer et al., 2003). Since subsurface tiles provide a conduit for nutrient export, treatment wetlands could function as temporary storages for tile discharge, and thus can help reduce agricultural impacts on downstream water quality. From 1994 – 1997, Kovacic et al. (2000) monitored N and P removal rates from wetlands receiving tile drain water in Illinois, and reported a 47% reduction for $\text{NO}_3\text{-N}$ and 2% reduction for TP. The authors suggested the wetland performed poorly in terms of P retention since this study measured inflow nutrient concentrations from the tiles only and did not account for P entering the wetland associated with sediment from surface runoff (Kovacic et al., 2000). Wetlands intercepting runoff in tile drained systems can receive nutrients from different areas on the landscape; NO_3^- runoff occurs via surface and subsurface flow while P export mainly occurs via surface runoff (Verehoeven et al., 2006).

Seasonal trends in nutrient export coupled with wet/dry rainfall cycles could also affect nutrient processing in treatment wetlands of the Midwest. Corstanje and Reddy (2004) conducted a laboratory study to assess the responses of Florida wetland soils to wet/dry cycles. After an 8 month drying period to simulate water table drawdown, soil cores from 2 sites, a nutrient enriched site and an undisturbed site, were subjected to

flooding. Biological activity, microbial biomass, enzyme activity, and nutrient release (nitrate and SRP) were found to substantially increase upon flooding. Stimulation of activity was greater in the core from the nutrient-rich site than in those from the undisturbed site. Nitrate flux was found to gradually decrease over the 30 day monitoring period in both undisturbed and enriched soils, whereas SRP decreased exponentially during the first 15 days of the study and then stabilized thereafter (Corstanje and Reddy, 2004). The authors attributed the initial increase in nutrient flux to enhanced mineralization of organic matter during water table drawdown. While informative, it should be noted that this and many other similar studies (Aldous et al., 2005; USEPA, 1993; Fisher and Reddy, 2001) were conducted with soils rich in organic matter ($> 20\%$ C), which is not typical for wetlands constructed on Midwestern croplands ($2\text{--}3\%$ C). In addition, many of these studies have not considered the variability in climate which can impact nutrient processing and fluxes. According to several climate change models (Kothavala, 1997), wet/dry rainfall cycles in the Midwest could become more intense. Specifically, these models predict that rainfall and drought patterns in the Midwest could intensify; although total rainfall will likely increase, it is predicted that short periods of excessive rainfall followed by periods of drought will become more frequent (Kothavala, 1997). At the present, it is unclear how treatment wetlands in the Midwest would withstand these changes in local climates and hydrologic regimes.

The capacity of treatment wetlands to process and retain nutrients is dependent on soil conditions and this can be dictated by antecedent land-use. As a result of many years of fertilizer application and/or pasturing, the surface layers of croplands can become

enriched with nutrients compared to adjacent forested soils (Koerner et al., 1997). Further, due to its relative low mobility, P enrichment in cropland surface soils can be quite pronounced (Compton and Boone, 2000), and this enrichment could have a large impact on P dynamics in newly constructed wetlands in agricultural landscapes. In light of these considerations, it is conceivable that a treatment wetland built on soils containing large pools of nutrients due to past agricultural activities may not have an immediate positive impact on water quality. During a two-year study, Liikanen et al. (2004) reported an average TP removal of 68% at an agricultural wetland receiving high nutrient runoff in Finland. The authors (Liikanen et al., 2004) proposed that this high P removal rate was due to scrapping off the topsoil layer prior to wetland construction allowing runoff to interact with Fe and Al-oxides present in the subsurface and which are known to be effective sites for P sorption. Although the removal of topsoil can improve P retention in wetlands built on former cropland, due to economic reasons this is not always a viable option in very large wetland systems. For instance, a large treatment wetland in the South Florida Everglades built upon former agricultural soil containing substantial amounts of P was found to undergo a period of adjustment during the first year of operation with higher P concentrations in the effluent (0.8 mg P L^{-1}) than the incoming water (0.12 mg P L^{-1}) (Kadlec, 2005). This study showed that wetlands can become a source of P during their initial period of operation.

While the studies reviewed above (USEPA, 1993; Kadlec, 2005; Liikanen et al., 2004) illustrate the impact of soil P level on P dynamics (source/sink) in newly-constructed wetlands, high P loads have also been shown to affect N cycling. In a laboratory experiment performed on soils from a wetland impacted by 40 years of P

loading in Southeastern Florida, White and Reddy (2003) investigated relationships between P-enrichment and NO_3^- processing. Denitrification (the reduction of NO_3^- into N_2O and N_2 gas) potential was found to be greatest towards the inlet of the wetland ($\sim 20 \text{ mg N kg}^{-1} \text{ h}^{-1}$) decreasing towards the end of the transect ($\sim 10 \text{ mg N kg}^{-1} \text{ h}^{-1}$) further away from the inlet. A significant ($p < 0.01$) correlation was found between denitrification and TP which led the authors (White and Reddy, 2003) to conclude that P was the nutrient limiting denitrifying activity (White and Reddy, 2003). The results of this study suggest that wetlands built upon soils with high antecedent P may exhibit enhanced capacity for denitrification.

Nitrogen and Phosphorus Biogeochemistry

The transformation of N and P in wetlands depends on vegetation uptake, hydrology and complex interactions between biological, physical and chemical processes operating in wetland soils. Thus, in order to understand the fate of N and P in wetlands, it is necessary to examine the processes governing transformations of these nutrients. Wet (anaerobic) versus dry (aerobic) conditions can have measurable effects on these processes. The oxidation reduction potential (ORP, relative affinity for a chemical species to reduce or oxidize another chemical species) provides a relative measure of these aerobic and anaerobic conditions (Kadlec and Wallace, 2009). Oxidation reduction potential is high (more positive) under oxidizing conditions, and is low (more negative) under reduced or anaerobic conditions.

Nitrogen Cycling

The cycling of nitrogen in wetlands involves the transformation of inorganic and organic forms of N within the soil and overlying water column. An important step in this cycle is nitrification, the process by which NH_4^+ is oxidized into NO_3^- . Under anaerobic conditions, available NO_3^- can undergo denitrification- the process by which NO_3^- is reduced to N_2O and N_2 gas, and a major pathway of excess N removal in wetlands (Kadlec and Wallace, 2009). Wetlands offer a favorable environment for denitrification since this process mainly occurs under O_2 -limited conditions. Denitrification is carried out by bacteria which use NO_3^- as an electron acceptor and organic matter as an electron donor (Kadlec and Wallace, 2009). Denitrification has been shown to be directly influenced by the availability of organic carbon in wetland soils as demonstrated by reported relationships between soil organic matter and NO_3^- consumption (Davidsson and Ståhl, 2000). While it is generally assumed that denitrification activity is stimulated by increased C availability, the results of other studies suggested that organic matter availability may not always limit denitrification. Using riparian wetland soils, Casey et al. (2001) found that the addition of dextrose did not significantly increase rates of denitrification (unamended soils were 75% the rate of amended soils). Given the high organic matter content ($> 5\%$ OM), of the studied soils, Casey et al., (2001) concluded that denitrification was limited by NO_3^- instead of organic C availability.

In wetland soils, microbial activity can be maintained under an array of hydrologic conditions which in turn could affect NO_3^- removal. Decomposition of organic molecules by heterotrophic micro-organisms results in the production of CO_2 which can be used as an index of soil biological activity. In several studies, drying and

rewetting of wetland soils have been shown to stimulate microbial activity. In a wetland soil mesocosm study, Corstanje and Reddy (2004) reported increased NO_3^- removal and CO_2 production in soils subjected to water drawdown and subsequent re-flooding. The authors concluded that the initial NO_3^- flush was linked to organic matter mineralization as suggested by the parallel increase in CO_2 production (Corstanje and Reddy, 2004). The exponential decline in NO_3^- levels (from 10 mg L^{-1} to complete exhaustion in 1 month) observed during this study also demonstrated that flooding of wetlands previously subjected to dry conditions can stimulate microbial activity and enhance denitrification potential.

Phosphorus Cycling

The cycling of P in wetlands is driven by different processes and can be more complex than N cycling. In the nitrogen cycle, N can be removed via export of dissolved N to adjacent streams, plant uptake, and gaseous emission (N_2 and N_2O). While the conversion to N_2 gas is a permanent N removal mechanism, there is no similar mechanism in the P cycle (very little to no gas P byproducts). P removal is via export in solution, plant uptake, precipitation and adsorption onto mineral surfaces (Kadlec, 2005). Plant uptake of P is somewhat short-lived since microbial decomposition of dead plant biomass will eventually convert organic P into mineral P. However, sediment deposition and burial of plant material can lead to slow decomposition of biomass; thereby increasing a wetland's potential to permanently store P (Kadlec, 2005). Adsorption, the process by which soluble inorganic P is moved from pore water onto soil mineral surfaces, is considered the only long-term P removal mechanism because of the generally

low solubility of some phosphate minerals (Dunne and Reddy, 2006). Since the sorption capacity of soil minerals is finite, this is nonetheless a possible limitation for long-term P retention in treatment wetlands via adsorption. In order to sustainably remove P in wetlands, new P sorption sites must become available. Working with pond and wetland sediment, Song et al. (2007) reported significant decrease in soil P sorption capacity following drying and the release of 45 % of previously adsorbed P when these soils were flooded.

There are various forms of P in wetlands, both organic and inorganic. Total P (TP) in wetlands can be broken down into particulate P (PP), dissolved organic P (DOP), and soluble reactive P (SRP) with the latter fraction being the bioavailable form of P. The particulate and organic forms of P have to undergo biological transformation in order to become bioavailable (Dunne and Reddy, 2006). This transformation is mediated by phosphatase, an enzyme system that breaks down the particulate and organic forms of P into mineral P. The activity of phosphatase has been studied under wet/dry conditions similar to wetlands which describe how this enzyme will possibly respond under the influence of enhanced P loads. In a study by Freeman et al. (1996), phosphatase enzyme activities in peatland soils significantly increased over an 18 week water table drawdown experiment compared to an unaltered wetland control. Since microbe respiration was not enhanced by water table drawdown, the authors could not link these outcomes to increased microbial activity. Instead, the authors (Freeman et al., 1996) speculated that increased enzyme activity during drawdown was caused by mobilization of enzymes attached to mineral surfaces and organic matter, termed the “reactivation hypothesis.” Using a slightly different hydrologic treatment, Corstanje and Reddy (2004) studied the

effect of water table drawdown and subsequent reflooding on phosphatase enzyme production and microbial activity. The authors found that phosphatase activity initially increased during the 30 day reflooding portion of the experiment, which coincided with anaerobic respiration rates. These two studies suggest that phosphatase enzyme activities can be enhanced by both water table drawdown and reflooding in wetland soils.

In wetlands with alkaline soils, Ca level determines inorganic P availability, whereas in acidic soils, Fe and Al control inorganic P solubility (Dunne and Reddy, 2006). Phosphate is negatively charged and attracted to positively charged cations (Ca^{2+} , Fe^{3+} and Al^{3+}) leading to P precipitation. Redox potential can also affect the solubility of Fe-bearing minerals and thus the availability of P in wetland soils. Under oxidizing conditions, Fe exists in the form of ferric iron (Fe^{3+}), whereas when the redox potential falls (more reducing conditions), Fe^{3+} is reduced to ferrous iron (Fe^{2+}). Thus, P adsorbed onto Fe-containing minerals could become mobile when Fe^{3+} is reduced to Fe^{2+} .

Since P retention is dependent on hydrologic conditions in wetland soils, there are many publications describing the impact of drying and flooding soils and its impact on nutrient retention in both laboratory and field investigations. Aldous et al. (2005) performed a laboratory experiment using restored and natural wetland soils to measure P release when soils were maintained under different hydrologic regimes including flooded, moist and dry followed by reflooding. Results showed that soils from restored wetlands released P under all hydrologic conditions, with the largest release coming from flooded and dried soils (Aldous et al., 2005). Phosphorus release following flooding was explained by the presence of high Al- and Fe-bound P fractions in both natural and restored wetland types. The authors attributed P release to changes in redox potential.

Under flooded conditions (lower redox potential), Fe^{3+} was reduced to Fe^{2+} and P originally bound to Fe-minerals was therefore released into the water column. It was further speculated that mineralization of organic P during the dry treatment could be a second factor contributing to P release upon flooding (Aldous et al., 2005) but information on dissolved organic P and phosphatase activity was not provided. Soils used in that study had high organic matter content (mean: 20% C) which is very high compared to Midwestern soils ($\leq 5\%$ OM). Due to the high OM content, it is possible that the results of this study are not entirely applicable to wetland soils of the Midwest.

One other study has shown that the rate at which water is added to dry or moist soils can also affect P mobilization in a laboratory setting. Blackwell et al. (2009) collected soils from the United Kingdom to examine how P concentrations changed after adding water at different rates to moist and dried soils. Dried soils released significant amounts of dissolved P in all (TP, inorganic and organic P) forms during the first rewetting period (2 hours after initial rewetting) compared to field moist soils. These results showed that rewetting dry soils can enhance P release compared to moist soils. A faster rate of water addition also increased dissolved P release during the initial rewetting period for dried soils, indicating that dry antecedent soil conditions have the potential to release P during intense rainfall events (Blackwell et al., 2009).

While these studies illustrate the high variability of P dynamics in soils exposed to different wet and dry conditions, most of these were performed in a laboratory setting. Russell and Maltby (1995) measured the effect of drying and subsequent flooding on ORP, oxygen, P, and Fe concentration in porewater samples in a riparian wetland exposed to agricultural runoff. This field experiment took place over 5 months (June-

November) beginning after a relatively dry spring and continuing through the course of a wet summer and fall. Results showed that E_h and oxygen concentration followed the inverse of the water table, decreasing as water table elevation increased. Thus anoxic or reduced conditions rapidly occurred during the first 6 weeks of the experiment. The highest P concentrations in porewater samples were observed during the initial “wetting up” phase of the experiment. Dissolved Fe concentrations were initially very low and did not follow trends in P concentrations as hypothesized by the authors. Since Fe and P did not follow similar trends, the authors suggested that oxygen concentrations could explain high initial P values. Oxygen concentrations during the initial rewetting were high enough to allow sustained microbial activity once the soil was rewetted, therefore enhancing organic carbon turnover and subsequent release of mineral P (Russell and Maltby, 1995). This study showed that P release may not always be linked to dissolved Fe concentrations.

Project Significance

Based on review of past and recent literature, there has been little research focusing on N and P cycling in wetlands built upon agricultural land that for decades had received large amounts of fertilizer and became nutrient enriched. Such wetland systems are likely to be common in agricultural landscapes of the US Midwest. Many studies on nutrient dynamics in wetland soils have been conducted in areas where soils contain very high levels of organic matter (e.g. peatlands) which is not typical for Midwestern soils. The Midwest is the greatest contributor of N and P pollution to the Mississippi River delta due to its agricultural practices (Turner and Rabalais, 2003). By understanding the

biogeochemical processes occurring in soils impacted by agriculture, scientists will be able to improve N and P retention in wetlands built upon these types of soils. While the necessity for improved water quality intensifies as greater pressures are being placed on agricultural systems, the need to understand and improve wetland nutrient processing in agricultural areas also continues.

Research questions and Hypotheses

1. How do antecedent soil conditions influence P and N fluxes in wetlands built upon agricultural soil?

For wetlands built on agricultural soils, antecedent soil conditions will directly affect P retention. It is hypothesized that P flux during flooding will be directly related to total soil P and the amount of P associated with Fe oxides. Thus, since P tends to accumulate in the surface layers of cropland and given the greater availability of P sorption sites in the subsoil, the removal of the topsoil prior to wetland construction should result in greater P retention in newly constructed wetlands.

2. How does change in hydrologic regimes (wet/dry cycles) affect P and N dynamics in constructed wetlands? Does the response to altered hydrology vary with antecedent soil conditions?

When exposed to drying conditions, a fraction of the organic matter in wetland soils will undergo mineralization and this will result in a flush of mineral P and N (available for export) once the wetland is flooded. Continuous flooding will also cause

the release of oxide-bound P via reductive dissolution. A significant linkage between P release and dissolved Fe is thus expected.

N removal in flooded wetlands will be related to the wetland's ability to sustain denitrification as determined by the availability of organic carbon and redox conditions. Upon flooding of dried wetland soils, the concentration of NO_3^- is expected to decrease progressively as anoxic conditions develop. Both the release and the removal of NO_3^- are expected to vary with antecedent soil conditions, being more vigorous in soils with large amounts of organic matter.

Research Objectives

1. Investigate the biological, physical, and chemical processes controlling N and P cycling in wetlands built upon agricultural soils.
2. Examine how different hydrologic conditions (dry/wet) influence nutrient release in agricultural wetland soils.

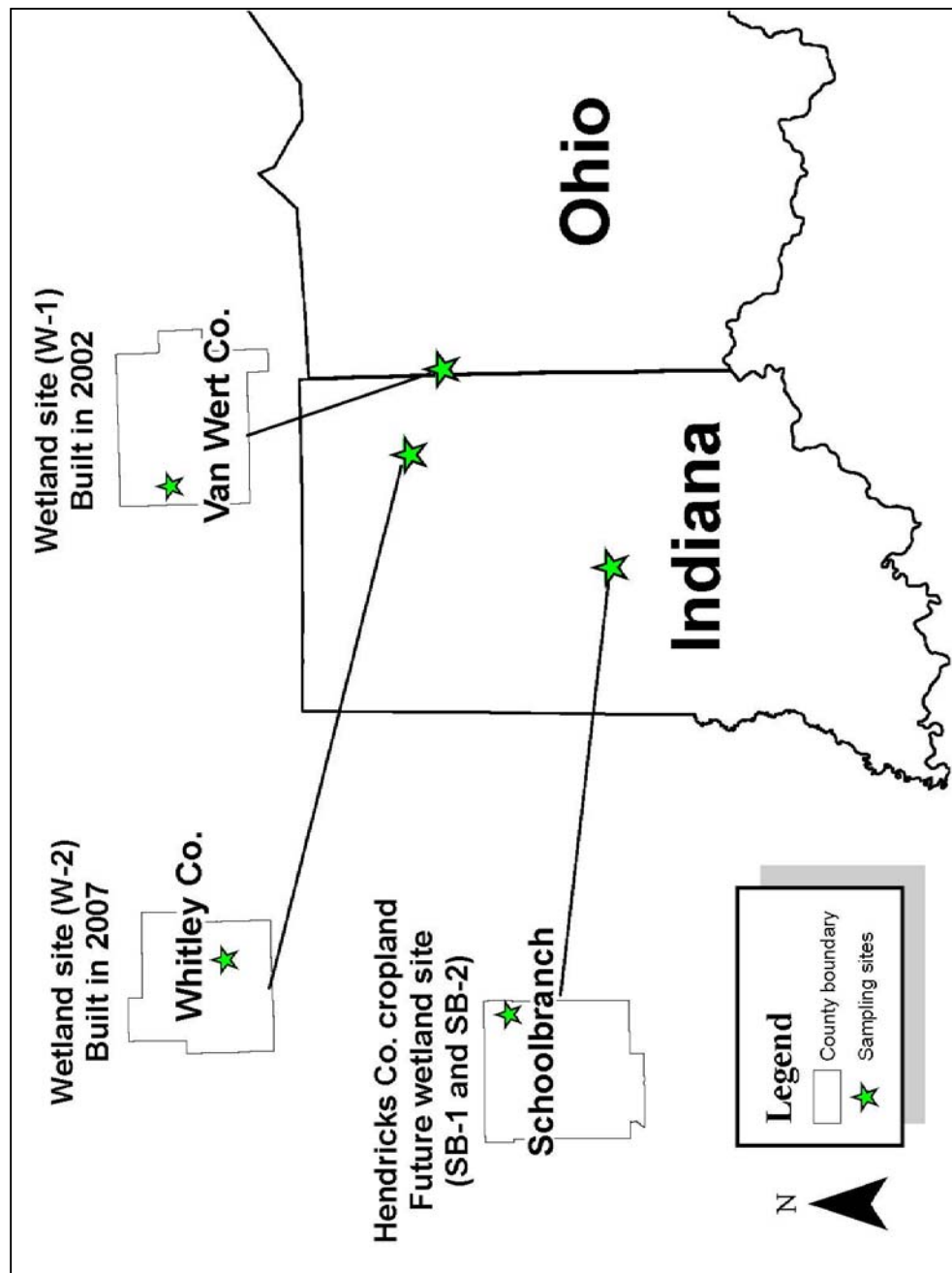
MATERIALS AND METHODS

Site Description

Soils were collected from 3 locations: 2 wetlands constructed on former croplands and 1 cropland where a wetland will be constructed in the future (Fig. 1). The first wetland (40°53' N, 84°45' W), located in Van Wert County, Northwest Ohio, was constructed in 2002. The second wetland (41°5' N, 85°26' W), established in 2006, is located at the Northeast Indiana Purdue Agricultural Center (NEPAC) in Whitley County, Northeast Indiana. The third site is a current cropland located in the Schoolbranch watershed in Hendricks County, Central Indiana (39°53' N, 86°21' W). Soils at these sites are mostly poorly drained silt and silty clay loams developed from Wisconsin glacial till underlain by dolomite and limestone bedrock. The sites are located within the Central Ohio till plain (Van Wert County), Bluffton till plain (NEPAC), and Tipton till plain (Schoolbranch cropland) physiographical regions (NRCS, 2006).

Soil cores were taken from the topsoil layer (0-20 cm) at all three sites. In addition, soil cores from Schoolbranch were taken from the subsurface layer (40-60 cm), all within the same soil pit. Since the Schoolbranch site will become a wetland in the future, the purpose of obtaining surface and subsurface soils was to determine the effect of antecedent soil conditions on nutrient release once a wetland is established. Hereafter, the sites will be referred to as: W-1 (Van Wert Co.), W-2 (NEPAC), SB-1 (Schoolbranch 0-20 cm) and SB-2 (Schoolbranch 40-60 cm).

Figure 1. Location of study sites. Cores were collected from 2 current wetlands and 1 cropland site for which surface (0-20 cm and subsurface (40-60 cm) cores were collected. Site name, date of construction of wetlands, and associated abbreviation used throughout the document are located above each county. Stars inside counties indicate exact location of sites.



Background Soil Properties

While collecting the large cores (10x20 cm), small cores (5x10 cm) were taken for determination of bulk density, and composite soil samples were collected for assessing chemical and biochemical soil properties including pH, texture, water extractable nutrients, total C, N, inorganic and organic P and P fractionation (water extractable, bicarbonate extractable and oxide-bound P). Dissolved organic C (DOC), dissolved organic P (DOP) and rapidly-desorbable P (RdP) were extracted using a soil suspension (10 g soil, 20 mL deionized water), shaken for 1 hour and centrifuged for 30 min at 4,000 rpm (Burford and Bremner, 1975; Pailles and Moody, 1992). The supernatant was filtered using a 0.45- μ m nylon fiber filter (Sartorius Stedim) and the filtrate frozen until analysis.

To determine bulk density, small (5x10 cm) cores were dried for 8 weeks to reach a constant weight. Bulk density was computed as the ratio of core dry weight to core volume. Soil pH was measured with a pH meter (Accumet 25, Fisher Scientific) using a soil suspension (2:1 water: soil ratio). Total soil P was determined by ashing oven dried (105 °C) soil samples in a muffle furnace at 550 °C for 1 h. This method converted all organic P to inorganic P, following the procedures by Anderson (1976). Residues were extracted with 25 mL 1N HCl for 15 min. over a hot plate. The extract was then diluted to 100 mL and the resulting solution concentration was determined using molybdate colorimetry.

The Hedley procedure (1982) was used to determine various P pools based on the relative solubility of soil P in water, alkali and acid solutions. Using 0.5 g field moist sample, all fractions were sequentially extracted using 30 mL of each reagent for a period

of 16 h and filtered (Whatman 42). The concentration of P was measured using molybdate colorimetry, using the extraction solution as the matrix in preparing the calibration curves. The extraction procedure was as follows: water extractable inorganic P (P_i) (WEP), moderately labile (P_i) extracted with 0.5 M NaHCO_3 , Fe/Al-bound P_i extracted with 0.1M NaOH, and Ca/Mg-bound P_i extracted with 1 M HCl (Hedley and Stewart, 1982, Qualls and Richardson, 1995). The first 2 fractions were more labile, while the last 2 fractions were generally considered recalcitrant.

Experimental setup and treatments

At each site, three sampling areas were randomly selected to capture natural site spatial variability. Random core selection was made by overlaying an approximately 10x10 m grid over aerial photography. Each 10x10 m grid was numbered and site selection was determined using a random number generator. In certain instances, discretion was made due to accessibility of some areas within each wetland due to high water tables. Within each 10x10 m sampling area, soil cores were collected in triplicate. A total of 6 cores were removed from each of the 2 wetland sites (0-20 cm depth), and 12 were collected from Schoolbranch (0-20 cm and 40-60 cm depth), for a total of 24 cores. Soil cores were encased in PVC pipes (40 cm length, 10 cm diameter) leaving 20 cm of headspace to accommodate a bottom cap and overlying treatment water. To collect core samples, the PVC pipes were driven into the soil to a depth of 20 cm. Cores were removed by digging out around the base and then cutting the bottom flush with a knife as to not disturb the core. The outer bottom edge of the PVC pipes were beveled to allow easier insertion into the soil and to minimize compaction. After removal, the bottom of

each core was gently pushed upward 3 cm to accommodate a 10 cm diameter water-tight PVC plug (Cherne Industries, Minneapolis, MN). Cores were transported to the laboratory, covered at the top with parafilm and stored at 4 °C until used in the greenhouse experiment described below.

The experiment was split into 2 phases and cores were subjected to 1 of 2 different treatments (dry or moist). During phase I, 3 cores from each site (total of 12 cores) were dried under ambient air temperature in a greenhouse for a period of 5 weeks (dry treatment). The remaining 12 cores were stored at 4 °C (moist treatment). One day before the start of phase II, the moist treatment cores were brought to uniform moisture content using deionized (DI) water.

During phase II, all dried and moist cores were flooded to a depth of 7 cm above the soil surface for an approximate headspace water volume of 560 mL. Cores were covered with parafilm to reduce evaporative water loss while allowing gas exchange. Water used to flood cores came from a ditch near the Van Wert, OH site. Chemical characteristics of the ditch water were expected to be typical of runoff waters entering wetlands from these areas. Concentrations of measured species from the ditch water (Table 1) were comparable to concentrations measured in shallow ground and surface water from Central Indiana (Vidon and Smith, 2007). Stream water was transported to the laboratory in 9.5 L collapsible LDPE plastic containers, filtered (20 µm), and stored frozen (-2°C) until used.

Chemical Species	Concentration (mg L ⁻¹)	Chemical Species	Concentration (mg L ⁻¹)
NO ₃ ⁻	0.23	Na	31.8 ± 0.57
NH ₄ ⁺	0.30	Ca	12.7 ± 0.07
SRP	0.03 ± 0.01	Mg	18.9 ± 0.25
DOP	0.06 ± 0.01	Fe	0.18 ± 0.01
DOC	16.6 ± 2.1	K	1.3 ± 0.27

Table 1. Stream water chemical composition used to flood cores during Phase II. Stream water used to flood cores during the experiment was taken from a drainage ditch at the Van Wert County, Ohio site when cores were sampled. Below is the chemical composition of the ditch water. Standard deviations are means of n=3.

During Phase II, water chemistry and nutrient fluxes in the flooded cores were measured on days 2, 5 and approximately every 7 days thereafter, for a total of 6 sampling events. During each sampling event, 35 mL of headspace water was removed from all cores using a syringe. Likewise, when accessible, porewater samples (15 cm depth) were extracted through a sampling port connected to an evacuated glass vial via a stopcock-syringe assembly (see below for complete description). All surface water samples were analyzed for dissolved SRP, organic P (DOP), DOC, DON, NO₃⁻, NH₄⁺, Fe, and acid phosphatase enzyme activity (APA). Porewater samples were analyzed for SRP, Ca²⁺, Mg²⁺, Na⁺ and K⁺. Any visible algae and plant material growing inside the cores during the experiment was removed prior to sampling. Due to excessive algal and macrophyte growth after 2 weeks of the experiment, removal of biomass occurred twice a week.

Carbon dioxide and N₂O production was also measured within 24 h of each sampling event. To measure gas production, core headspace was closed with water-tight PVC plugs (Cherne Industires, Minneapolis, MN) equipped with a rubber septum

sampling port. Approximately 15 mL air samples were taken from the headspace using a syringe and transferred into evacuated glass vials. This procedure was repeated until three samples were taken at 0, 30 and 60 min intervals.

Variations in pH and ORP in the floodwater (headspace) and porewater (subsurface) were monitored using pH and ORP probes (Fisher Scientific, model 300731.1 and 300746.0, respectively). In the floodwater, these measurements were made by placing the probe half way between the water surface and the soil/water interface in the center of the core. In order to measure subsurface porewater ORP, cores were outfitted with a sampling port (15 cm depth through the PVC casing). The sampling port was made from 1.5 mm diameter low permeability FEP-lined plastic tubing (Catalog # 6406-32, Cole Parmer), perforated and covered at its inner end with 20 μ m nylon membrane, and plugged at the outer end with a two-way stopcock. To create the sampling port, a hole was drilled on the side of the PVC casing at a depth corresponding to 15 cm below the soil core surface. The sampling port was secured to the PVC pipe using caulking and waterproof Marine Goop. Subsurface pore water samples were extracted from the cores using a syringe attached to an evacuated glass vial. Once the desired volume was obtained, the ORP probe was then quickly and firmly screwed to the glass vial to avoid air exchange. Due to slow soil pore saturation and sampling port clogging problems, porewater sampling began on Day 19 (half way through the experiment).

Analytical procedures

Total C (TC) and total N (TN) was measured by dry combustion (950 °C) using a Vario TOC Cube analyzer (Elementar Inc., NJ). Total dissolved N (TDN) and DOC was also analyzed using the Vario TOC Cube analyzer.

Soluble reactive P (SRP) was determined using molybdate colorimetric method described by D'Angelo et al. (2001). Quadruplicate 100 μL aliquots of each sample were transferred to a 96 well microplate. Each well then received 40 μL of 14.2 mmol L^{-1} ammonium molybdate tetrahydrate in 3.1 M H_2SO_4 . After waiting 10 minutes, a 40 μL mixture of 3.5 g L^{-1} polyvinyl alcohol (PVA) and 0.35 g L^{-1} malachite green were added to the wells. After 20 minutes to allow color development, the absorbance ($\lambda = 630 \text{ nm}$) of the resulting solution was read on a spectrophotometer (Versamax, Sunnyvale, CA). A standard curve using solutions of known P concentrations versus absorbance was also prepared. From the line equation of the standard curve, SRP concentration was determined for all samples. Filtered samples not run within 48 hours were frozen for future analysis.

Using 10 mL of the same soil supernatant extracted above, the total dissolved P (TP) was determined by oxidizing organic P into inorganic P by autoclaving the sample at 110°C for 30 min in the presence of 13.4 g L^{-1} potassium persulfate dissolved in 0.3M NaOH. The concentration of P in the autoclaved solution was determined using the molybdate colorimetric method described above. Phytic acid solutions of known P concentrations were also autoclaved and analyzed to assess percent P recovery of the autoclaving method (Williams et al., 1995). The difference between TP and SRP was used to estimate DOP.

Headspace water samples removed during Phase II were immediately filtered using a 45- μm nylon filter and analyzed for SRP, TP, DOC, NO_3^- , NH_4^+ , dissolved Fe, Ca^{2+} , Mg^{2+} , Na^+ and K^+ . DOC, TP and SRP analysis were run as previously indicated. Nitrate and NH_4^+ were run using an automated photometric analyzer (Aquachem 20, EST Analytical, Fairfield, OH) using EPA standard methods 350.1 and 375.4 (Clesceri et al., 2002). Dissolved Fe and major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Leeman Labs, Hudson, NH). Analysis of air samples for CO_2 , N_2O , and CH_4 were conducted on a Varian CP 3800 gas chromatograph.

Acid phosphatase enzyme activity (APA) in the floodwater was measured within a few hours of sample collection. Using a 96 well microplate, methylumbelliferyl phosphate (MUF-P) substrate was added to water samples placed in the microplate wells and incubated at room temperature (22 °C) for 2 h in the dark. In each incubation batch, several blanks (MUF-P only, water only) were included to account for background fluorescence. After incubation, the reaction was quenched with 1 N NaOH and the microplates were run on a fluorescence reader (Cary Eclipse, Varian Inc., CA) with an emission wavelength of 447 nm, excitation wavelength 360 nm, and a PMT of 600 V. The rate of MUF production was taken as a measure of phosphatase activity of the floodwater in the soil cores. All reagents were obtained from Sigma.

Data Analysis

The amount of SRP and NO_3^- released per unit time was computed as the difference between concentration in the floodwater and initial concentration in the stream

water used to flood the cores at the beginning of phase 2. To calculate flux (F), this value was multiplied by the headspace water volume (V: 0.56 L) and then divided by the soil core surface area (A: 0.78 m²) and the time lapse (days) between consecutive sampling events. Nutrient flux was expressed in mg m⁻² d⁻¹ and computed using the following equation:

$$F = \frac{(C_t - C_i)V}{A t}$$

Where C_t is the concentration in the flood water, C_i is the concentration in the stream water (water added to the core), V is the core water volume, A is the surface area of the soil, and t is the time between sampling events.

The rate of gas produced (CO₂ and N₂O) was calculated as the slope of the line over the 60 minute sampling interval and converted to mg gas produced per m⁻² d⁻¹. Carbon dioxide data was used to determine if there was a correlation between DOC release and increases/decreases in CO₂ production. Nitrous oxide data was used to support changes in NO₃⁻ release (evidence for denitrification).

Relationships between P fractions, background soil properties and dissolved Fe (both in pore water and in floodwater) were analyzed to examine possible links with P release. Likewise, APA results were compared to inorganic P data to determine if there were any trends between enzyme activity and SRP release.

Statistical analysis

All data was analyzed using linear regression, analysis of variance (ANOVA) or t-tests to find statistical differences between sampling events, core treatments and soil sites. During this study, statistical procedures were performed with the consideration that

there were 2 treatments; dry and moist, and 4 sites; SB-1, SB-2, W-1, and W-2. Separate analysis of variance tests were run to determine if there are (1) statistical differences between treatments and (2) statistical differences between sites. T tests were run to determine if there were statistical differences between treatments during each sampling event.

Data were first analyzed for normal distribution. If data sets did not pass normal distribution tests, data transformations were performed. Natural log transformations were performed on Fe , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , NH_4^+ , and DOC data sets. Reciprocal transformations were used for the SRP and APA results, while square root transformations were performed on the DOP data. For normally distributed data, regular two sample t-tests were used to compare treatments within individual sites. For data that did not pass normality after transformations, non parametric methods were used (Mann-Whitney rank sum test). Correlations were performed using the Spearman rank order method. Two-way analysis of variance (ANOVA) was used to assess the effect of sites and treatments. One way ANOVA and Kruskal Wallance ANOVA on ranks were used to determine differences amongst background soil properties. A confidence level of $p < 0.05$ (statistically significant difference) was used for all tests.

RESULTS

Physical and chemical properties of soils

The soil pH at the study varied from 6.0 to 6.9 (Table 2a). Clay content at the W-1 and W-2 wetlands (clay loam) was higher than at the ST site (sandy clay loam). All sites had similar silt contents, ranging between 22 to 25% (Table 2a). Soil bulk density ranged from 1.1 g cm⁻³ (SB-1) to 1.4 g cm⁻³ (W-1).

Wetland 2 had the highest total C (TC) and total phosphorus (TP) content whereas SB-2 had the lowest amount of all bulk soil properties (Table 2a). Soil C content ranged from 1.24 to 2.70% with statistically significant differences ($p < 0.001$) detected amongst sites (Table 2a). Total N (TN) content ranged from 0.12 to 0.20% (Table 2a) with significantly ($p < 0.01$) higher amounts in SB-1 and W-2 compared to the SB-2 soil. The C/N ratio of soil ranged between 10.3 and 15, and was significantly higher in W-2 soils compared to the other sites. Total P content ranged from 331 to 570 g P kg⁻¹ soil, but no significant differences amongst sites were detected.

The amount of water extractable nutrients varied with site. Dissolved organic C ranged from 37 to 89 mg C kg⁻¹ soil, with the highest concentration measured in W-2 and the lowest in SB-1 (Table 2b). The pool of rapidly desorbable phosphorus (RdP, 2-h extraction) content was not significantly different among sites, and ranged from 0.20 to 0.27 mg P kg⁻¹ soil (Table 2b). However, dissolved organic P (DOP) levels varied with site. The lowest DOP pool was measured at SB-2 and W-2 (0.05 and 0.09 mg P kg⁻¹ soil, respectively) and the highest at W-1 and SB-1 (0.36 to 0.51 mg P kg⁻¹ soil, respectively). Site SB-1 had significantly higher DOP compared to all other sites (Table 2b).

Table 2a. Physical and bulk soil properties of the study sites. Values followed by different letters are significantly different at $p < 0.05$. Standard deviations are means of $n=3$.

Site	pH	% Clay	% Silt	Bulk Density (g cm ⁻³)	%C	%N	C:N Ratio	Total P (TP) mg P kg ⁻¹ soil
SB 1	6.9 ± 0.02 ^a	27 ± 1.2	25 ± 1.4	1.1 ± 0.1	2.17 ± 0.08 ^b	0.20 ± 0.02 ^a	10.9 ^a	570 ± 101 ^a
SB 2	6.9 ± 0.02 ^a	28 ± 2.6	22 ± 0.0	1.3 ± 0.05	1.24 ± 0.01 ^c	0.12 ± 0.01 ^b	10.3 ^a	331 ± 115 ^a
W 1	6.0 ± 0.01 ^a	36 ± 2.6	25 ± 1.4	1.4 ± 0.03	1.65 ± 0.09 ^b	0.14 ± 0.01 ^b	11.8 ^a	513 ± 158 ^a
W 2	6.5 ± 0.02 ^a	41 ± 4.0	27 ± 7.1	1.4 ± 0.02	2.70 ± 0.13 ^a	0.18 ± 0.03 ^a	15.0 ^b	443 ± 210 ^a

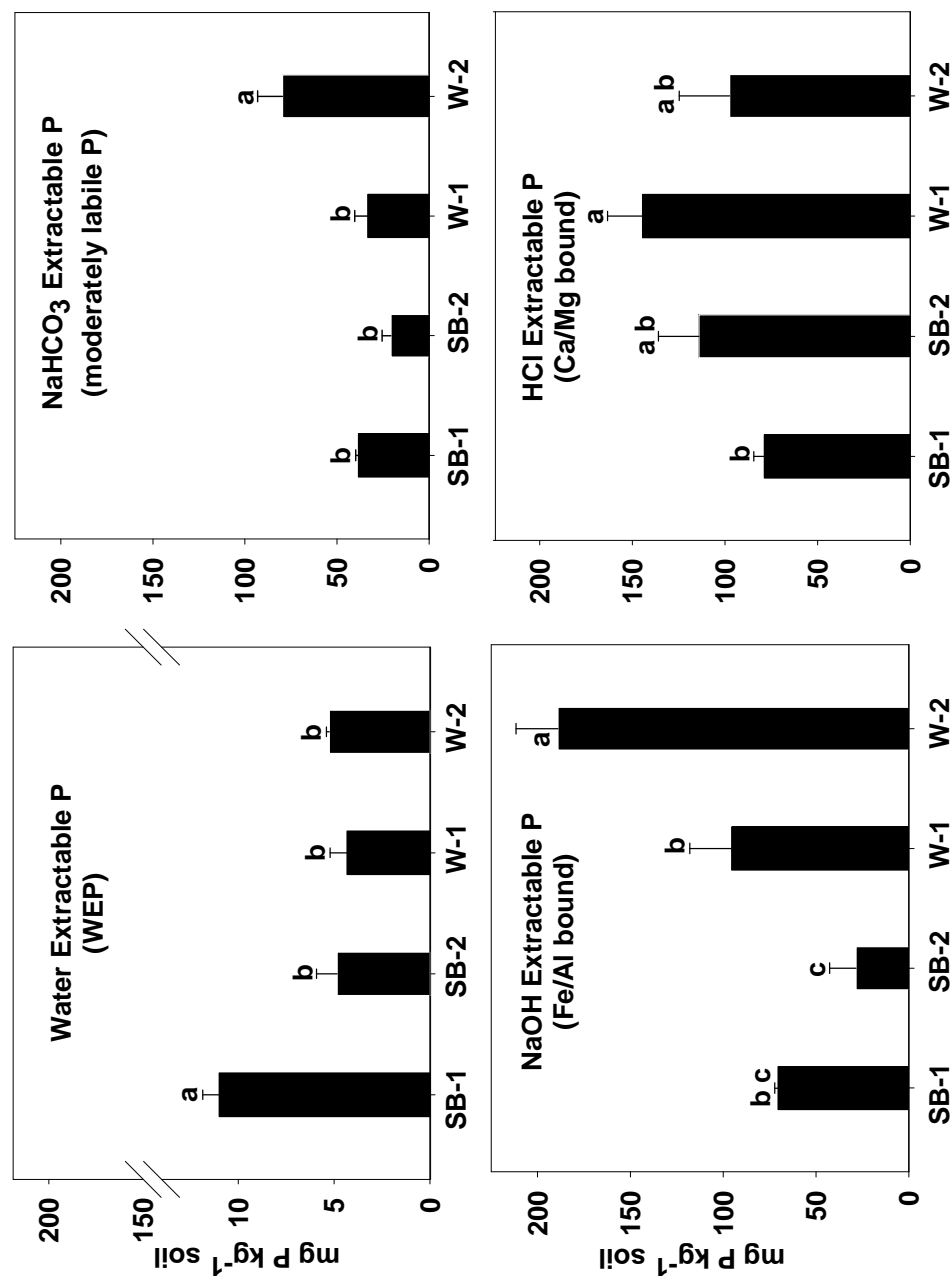
Table 2b. Water extractable nutrients of the study sites. Values followed by different letters are significantly different at $p < 0.05$. Standard deviations are means of $n=3$.

Site	Dissolved Organic Carbon (DOC) mg C kg ⁻¹ soil	Rapidly Desorbable Inorganic Phosphorus (RdP _i) mg P kg ⁻¹ soil	Dissolved Organic Phosphorus (DOP) mg P kg ⁻¹ soil
SB 1	37 ± 4.3 ^c	0.27 ± 0.05 ^a	0.51 ± 0.14 ^a
SB 2	63 ± 7.1 ^b	0.20 ± 0.03 ^a	0.05 ± 0.02 ^b
W 1	47 ± 7.0 ^c	0.21 ± 0.01 ^a	0.36 ± 0.04 ^b
W 2	89 ± 2.3 ^a	0.24 ± 0.0 ^a	0.09 ± 0.02 ^b

Sequential phosphorus fractionation

Although there was no significant difference in TP (Table 2a), or rapidly desorbable phosphorus (RdP) (Table 2b), the sites differed in terms of the distribution of P among the various pools as determined by the Hedley fractionation procedure. The SB-1 site had significantly higher 16 hr water-extractable P (WEP) compared to all other sites. Conversely, the NaHCO₃ and NaOH extractable P fractions were significantly higher in W-2 compared to all other sites (Fig. 2). The only statistically significant difference among sites with respect to HCl extractable P (Ca/Mg bound) was between W-1 and SB-1 (Fig. 2).

Figure 2. Sequential phosphorus fractionation of bulk soil. The same soil was sequentially extracted with the following solutions in this order: H_2O , NaHCO_3 , HCl , and NaOH . Different letters indicate a statistical difference at $p < 0.05$. Error bars represent standard deviations of $n=3$.



Concentrations of P, N and DOC in the floodwater

During the first week of the experiment, NO_3^- concentrations were significantly higher ($p < 0.05$) in the floodwater in the dry treatment cores compared to the moist treatment cores (Fig. 3). This initial increase in NO_3^- only lasted for a few days, however. In the dry W-1 and W-2 cores, NO_3^- rapidly decreased from 3.8 (W-1) and 2.2 (W-2) mg N L^{-1} to 0.23 mg N L^{-1} by Day 5 (Fig. 3). In contrast to the rapid NO_3^- concentration decline in cores from the wetland sites, the drop in concentration in the ST cores was more gradual. The spike of NO_3^- observed in the SB-1 cores (10.8 mg N L^{-1}) lasted until Day 19. In the SB-2 cores, the initial spike was less notable (2.7 mg N L^{-1}) but lasted until Day 29 (Fig. 3). After Day 29, there was no significant difference among all sites with respect to NO_3^- concentrations in the floodwater (Tables 3-8).

Figure 3. Floodwater dissolved NO_3^- concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

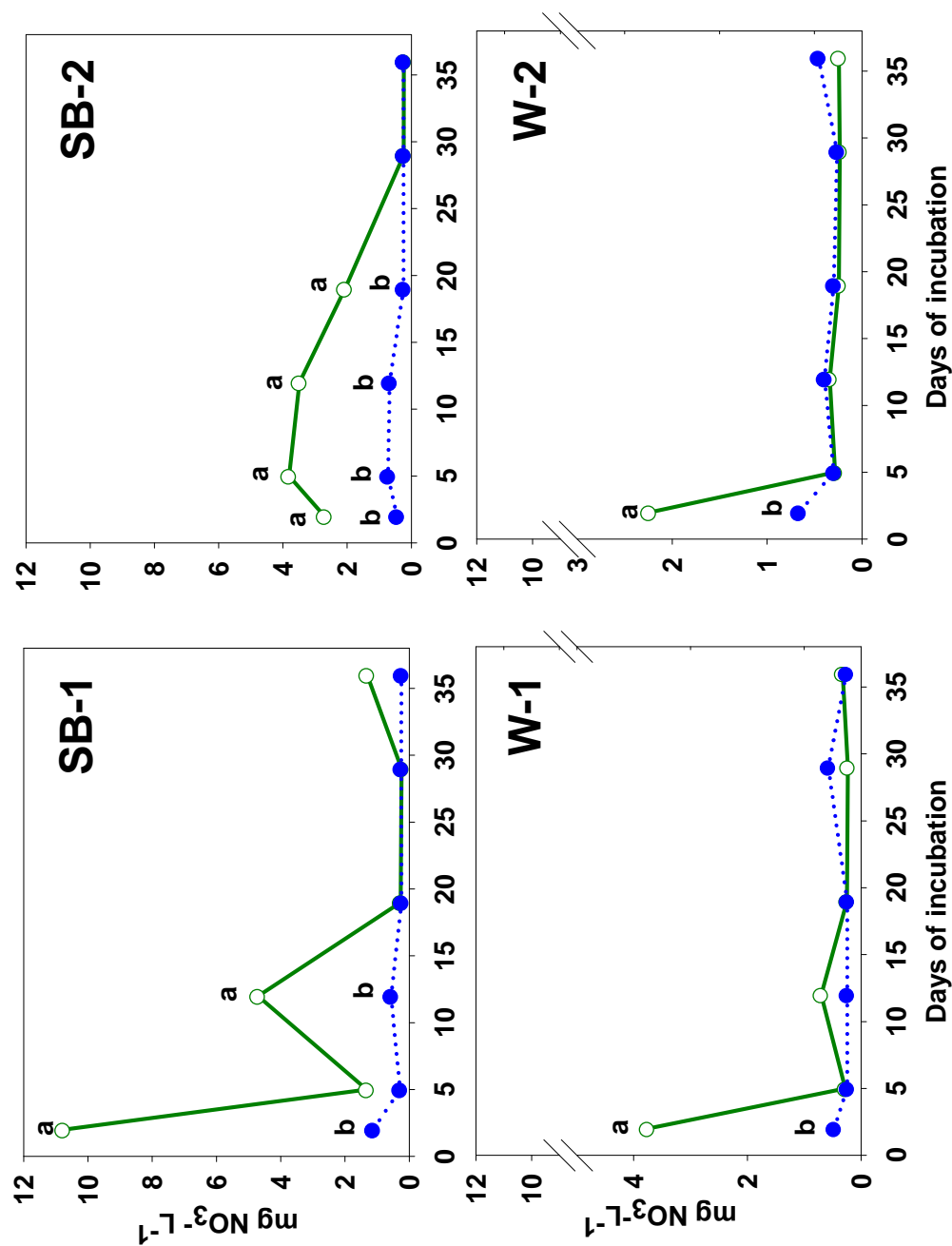


Table 3. Two-Way ANOVA results for Day 2 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	3	NS	NS	NS	**	***	NS	***	NS	***	***	***	***	*	NS
Treatment	1	NS	***	**	NS	NS	*	NS	***	NS	***	***	*	***	NS
Site X Treatment	3	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

Table 4. Two-Way ANOVA results for Day 5 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	3	NS	***	**	NS	*	***	***	**	***	***	***	NS	***	***
Treatment	1	*	**	NS	NS	*	NS	**	NS	***	***	*	***	***	NS
Site X Treatment	3	NS	NS	NS	NS	NS	NS	NS	NS	NS	**	NS	NS	***	NS

Table 5. Two-Way ANOVA results for Day 12 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	*	***	***	NS	NS	**	***	***	***	***	***	NS	**	**	*
Treatment	NS	***	*	*	NS	NS	***	NS	***	NS	NS	***	**	**	NS
Site X Treatment	NS	**	NS	*	NS	NS	*	NS	NS	NS	NS	NS	**	NS	NS

Table 6. Two-Way ANOVA results for Day 19 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	3	NS	*	*	*	ND	ND	**	NS	***	***	***	*	ND	ND
Treatment	1	NS	NS	NS	NS	ND	ND	NS	NS	**	NS	*	***	ND	ND
Site X Treatment	3	NS	*	NS	NS	ND	ND	NS	NS	NS	NS	NS	NS	ND	ND

Table 7. Two-Way ANOVA results for Day 29 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	3	**	NS	*	NS	NS	NS	***	**	***	***	***	NS	***	***
Treatment	1	***	NS	NS	NS	NS	NS	NS	NS	*	**	NS	***	NS	***
Site X Treatment	3	**	NS	NS	NS	NS	NS	NS	NS	***	***	NS	*	NS	NS

Table 8. Two-Way ANOVA results for Day 36 of the experiment. Abbreviations are as follows: APA = acid phosphatase activity, NO₃⁻ = nitrate, PO₄⁻³ = inorganic phosphorus, DOP = dissolved organic phosphorus, N₂O = nitrous oxide, CO₂ = carbon dioxide, DOC = dissolved organic carbon, ORP = oxidation reduction potential. * p<0.05, **p<0.01, ***p<0.001, NS = Not significant, ND= Not determined.

Response Variables															
Class Variables	df	APA	NO ₃ ⁻	PO ₄ ⁻³	DOP	N ₂ O	CO ₂	DOC	Fe	Mg	Ca	K	Na	ORP	pH
Site	3	NS	NS	NS	NS	NS	NS	***	***	***	***	***	*	***	***
Treatment	1	*	NS	NS	NS	NS	NS	NS	NS	NS	**	NS	***	NS	**
Site X Treatment	3	NS	NS	NS	*	NS	*	NS	NS	NS	NS	NS	NS	NS	NS

Patterns in ammonium (NH_4^+) concentrations were not as discernable as those observed with NO_3^- . There was no clear trend amongst sites or treatments; however, there were some noteworthy day to day variations. During the first 2 days of the experiment, the floodwater in the SB-1 dry treatment cores showed marked increases in NH_4^+ concentrations (Fig. 4) compared to the stream water (Table 1) used to flood the cores (+0.11 mg L^{-1} difference). In the SB-2 cores, NH_4^+ concentrations remained relatively constant after flooding regardless of treatment. In the W-1 and W-2 cores, NH_4^+ concentrations were highly variable in both treatments and did not follow any well-defined trends (Fig. 4). Due to this variability, NH_4^+ fluxes were not calculated.

Soluble reactive P concentrations in the floodwater were higher in the dry than in the moist treatment for SB-1 and SB-2 cores but, for most sampling dates; the difference was not statistically significant (Fig. 5). Sample water SRP in the dry treatment SB cores ranged between 0.19 (SB-2) to 0.84 (SB-1) mg P L^{-1} and gradually decreased to <0.10 mg P L^{-1} around Day 36 (Fig. 5). Regardless of treatments, the SB-1 cores released significantly more SRP compared to the other sites. The wetland sites released the lowest amounts of SRP and no effect of treatment was detected (Fig. 5).

Dissolved organic P concentrations in the sample water ranged from 0.07 to 1.3 mg L^{-1} (Fig. 6). There was no significant effect of site or treatment for the duration of the experiment, yet there was a significant increase in DOP from SB-1 on the last day of the experiment. No other statistical relationships were found between DOP and the other parameters measured.

When comparing the floodwater background DOC concentration (16.6 mg L^{-1} , Table 1), the initial DOC concentrations in the floodwater on day 2 increased in all of the

dry cores. In the moist cores; however, concentrations either remained stable or dropped. The most significant treatment effects were limited to the SB-1, W-1 and W-2 cores and to the first 2 weeks of the experiment (Fig.7). With the exception of the SB-2 cores, DOC concentrations generally increased as the experiment went on regardless of treatment.

Figure 4. Floodwater dissolved ammonium concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

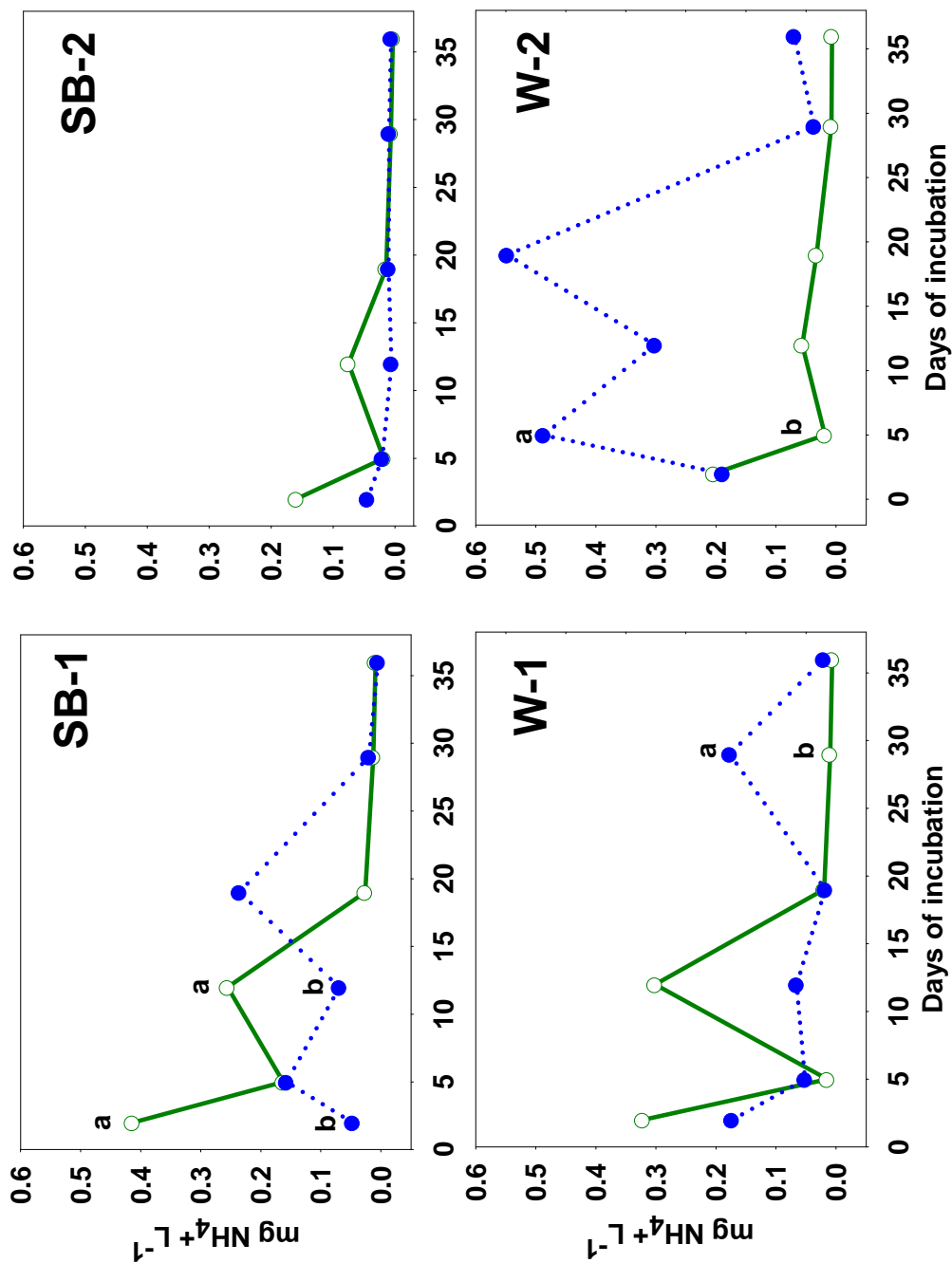


Figure 5. Floodwater dissolved soluble reactive phosphorus (SRP) concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

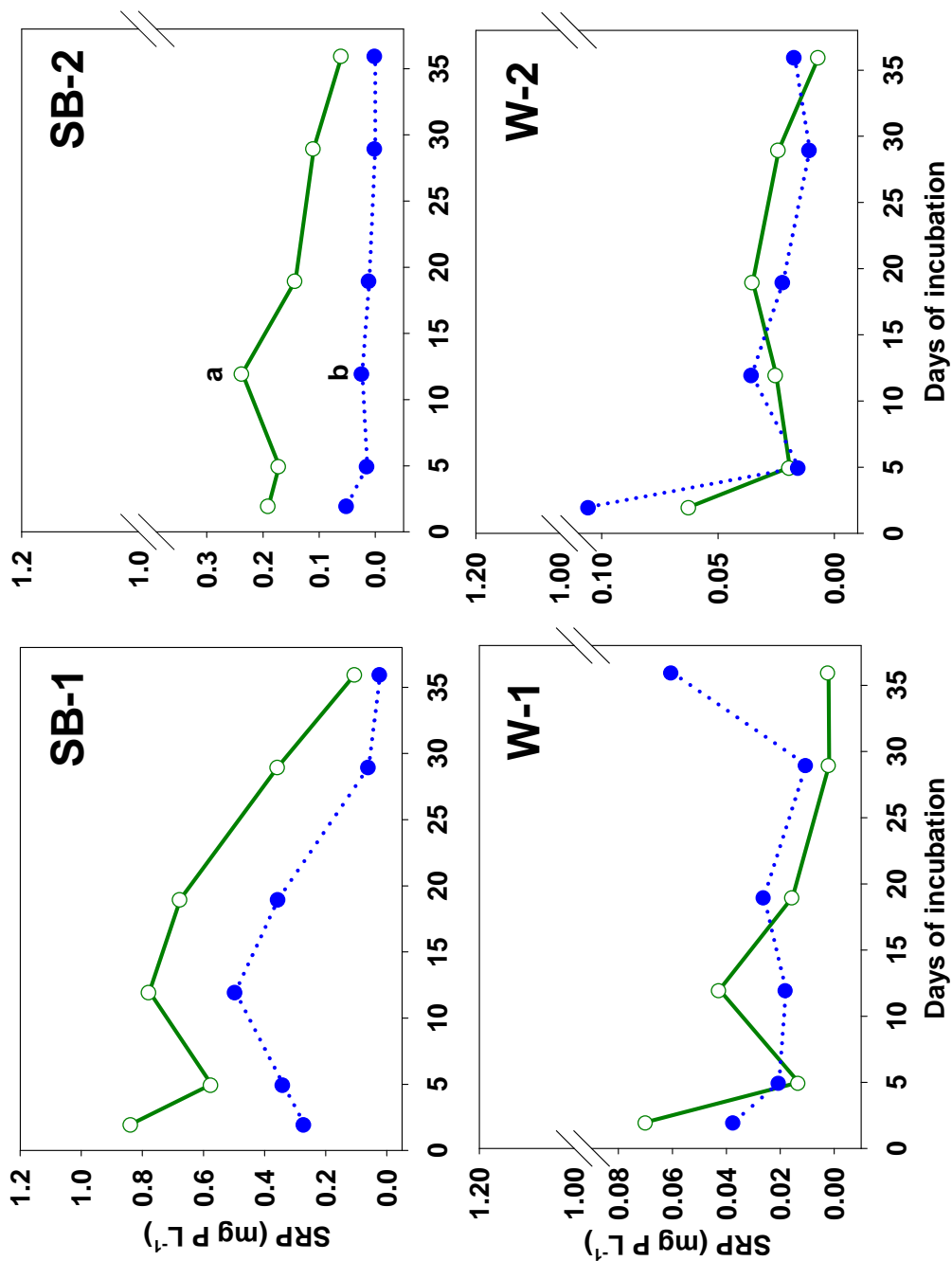


Figure 6. Floodwater dissolved organic phosphorus (DOP) concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

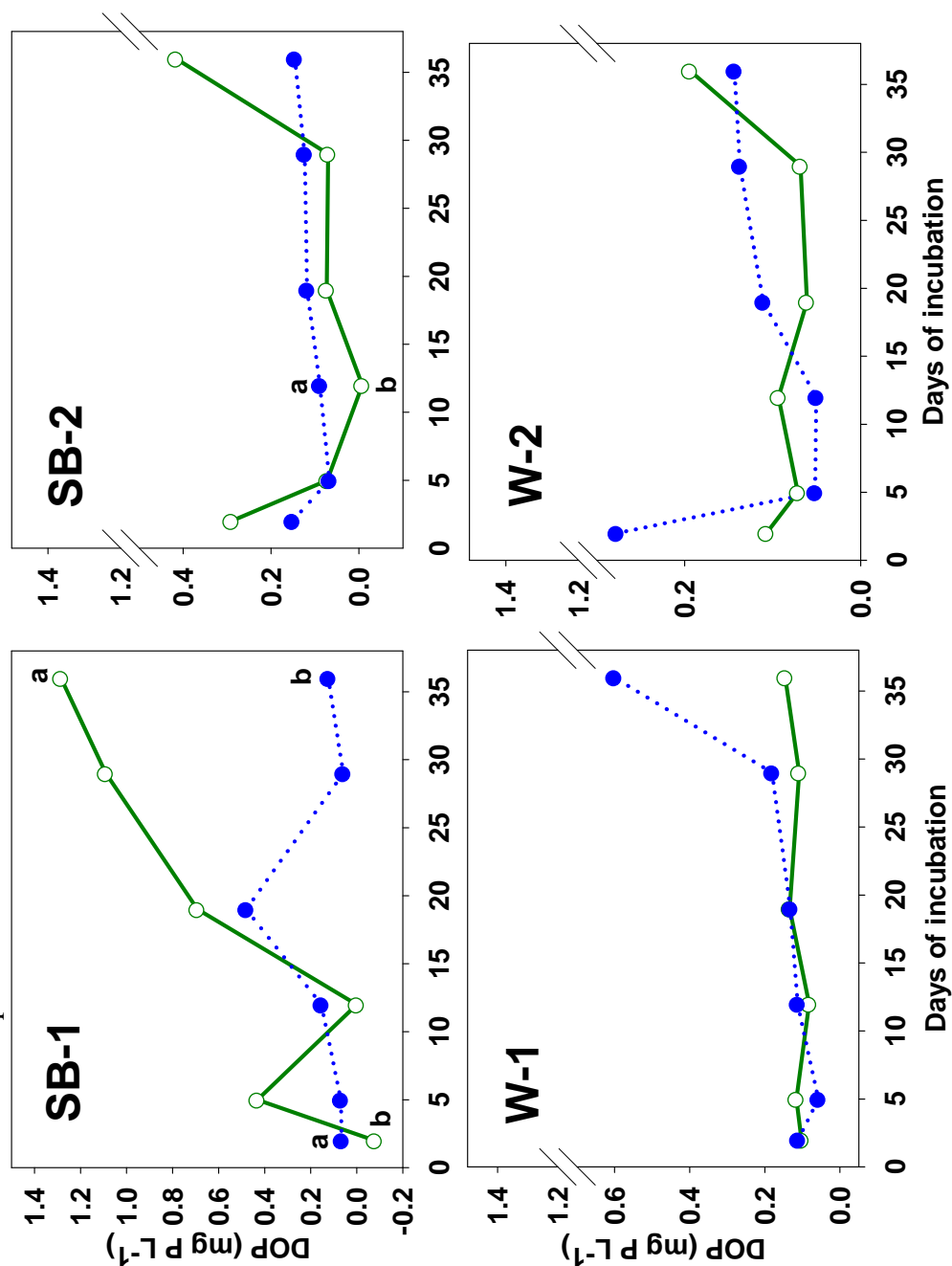
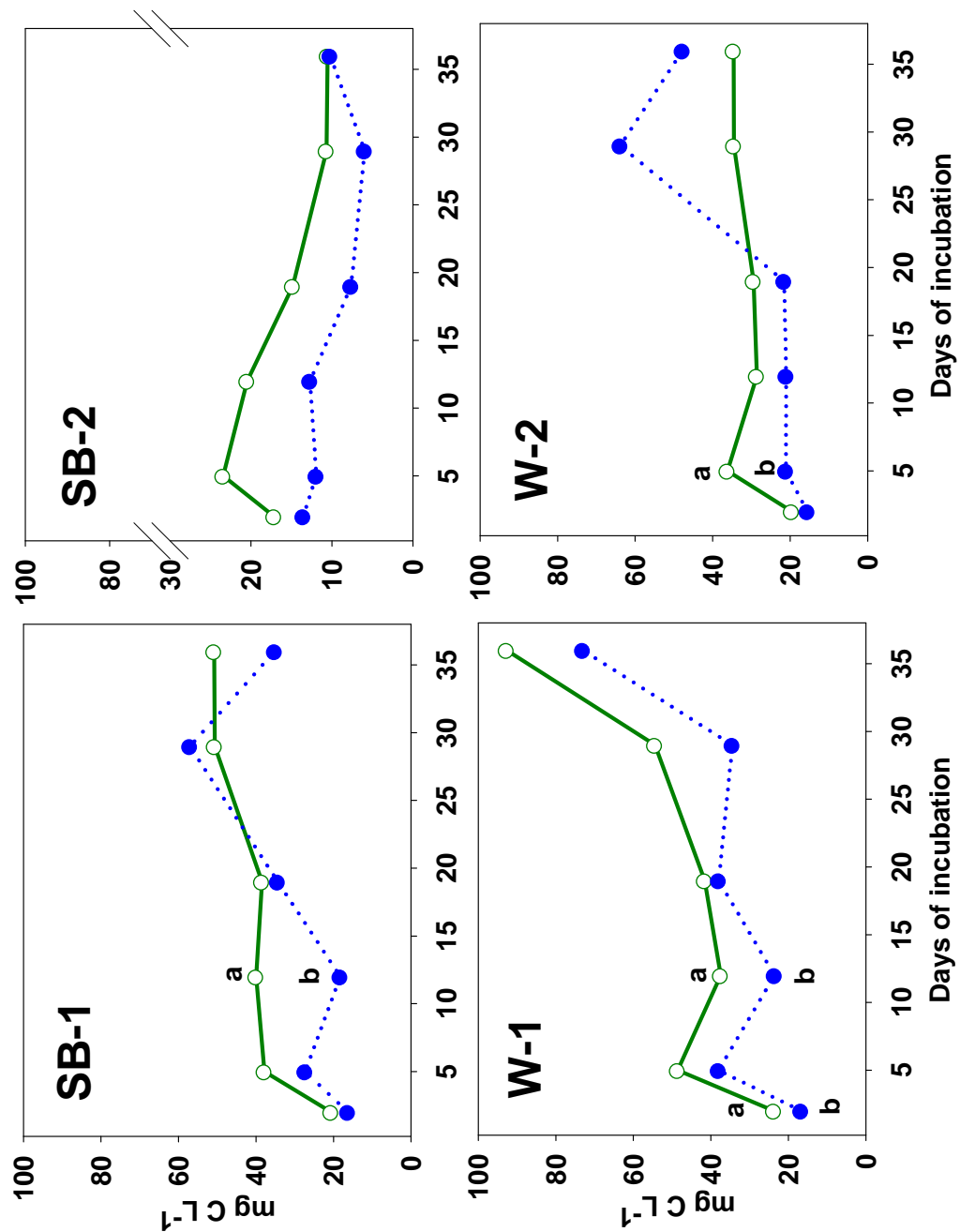


Figure 7. Floodwater dissolved organic carbon (DOC) concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



Nutrient Fluxes

Since most of the nutrient release occurred during the initial 2 weeks of the experiment, nutrient fluxes were calculated from the period of initial core wetting ($t=0$) to Day 12 ($t=12$). Two-way ANOVA results showed a significant effect of site ($p<0.05$) and treatment ($p<0.01$) on N fluxes (Table 9). Initial NO_3^- fluxes were higher in dry versus moist treatment cores for all sites (Fig. 8). The highest NO_3^- fluxes were observed in the SB-1 cores (mean: $130 \text{ mg N m}^{-2} \text{ d}^{-1}$), followed by the W-1 ($47 \text{ mg N m}^{-2} \text{ d}^{-1}$), the W-2 ($26 \text{ mg N m}^{-2} \text{ d}^{-1}$), and the SB-2 ($16 \text{ mg N m}^{-2} \text{ d}^{-1}$) cores. Moist treatment cores produced much lower NO_3^- fluxes, ranging from 0.1 to $4.4 \text{ mg N m}^{-2} \text{ d}^{-1}$ (Fig. 8).

Response Variables			
	df	NO_3^-	SRP
Site	3	*	***
Treatment	1	**	NS
Site X Treatment	3	NS	NS

Table 9. Two-Way ANOVA results for NO_3^- and SRP flux during sample Days 0-12.

* $p<0.05$, ** $p<0.01$, *** $p<0.001$, NS = Not significant

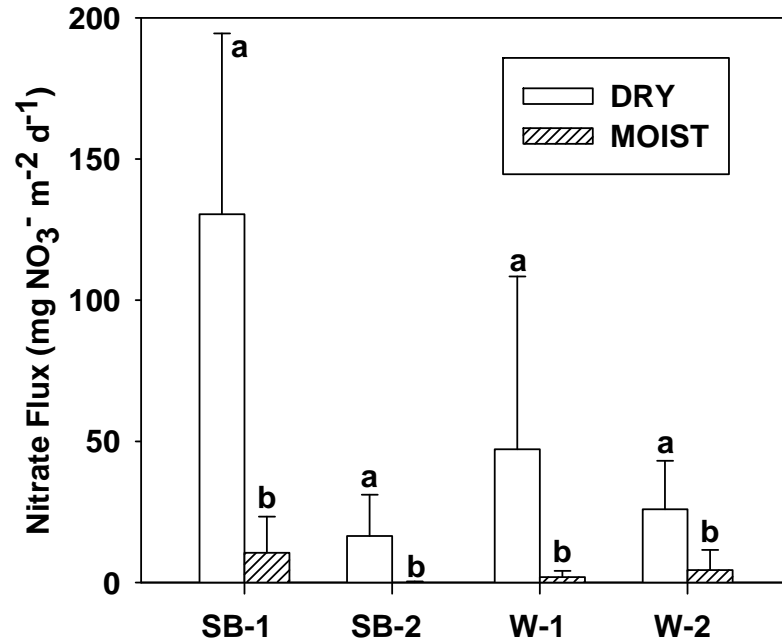


Figure 8. Nitrate flux of dry and moist treatments. Flux is calculated based on NO₃⁻ concentrations in the floodwater for the first 12 days of the experiment. Different letters between pairs indicate a statistical difference at $p > 0.05$.

Phosphate fluxes ranged from 0.09 to 2.9 mg P m⁻² d⁻¹ (Fig. 9) and the highest rates of P release were recorded in the SB-1 cores. ANOVA showed a statistically significant effect of site ($p < 0.001$) on P fluxes (Table 9). Upon further examination (based on the Holm-Sidak pairwise multiple comparison procedure), there was a statistical difference between treatments in the SB-2 cores ($p < 0.01$). Otherwise, the SB-2 moist cores released P at similar rates as the wetlands (Fig. 9).

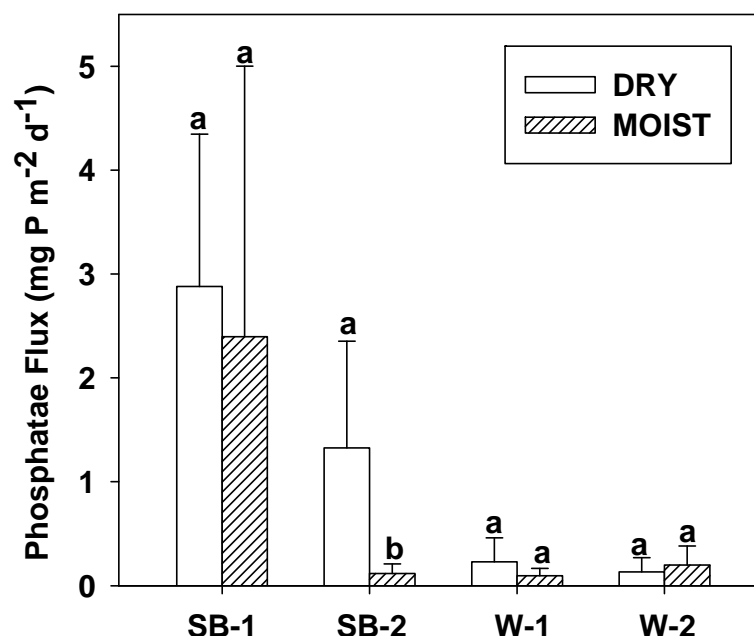


Figure 9. SRP flux of dry and moist treatments. Flux is calculated based on SRP concentrations in the floodwater for the first 12 days of the experiment. Different letters between pairs indicate a statistical difference at $p > 0.05$.

Dissolved cations in the floodwater and porewater

The concentration of dissolved cations (Mg^{2+} , Ca^{2+} and Na^{+}) in the floodwater was generally higher in the dry than moist treatment cores (Fig. 10-12). The effect of treatment K^{+} concentrations in sample water was less consistent (Fig.13). If the SB-1 and SB-2 data are considered separately, significant relationships were found in the floodwater with respect to DOC and dissolved Ca^{2+} and Mg^{2+} (Fig. 14-15).

Figure 10. Floodwater dissolved magnesium concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

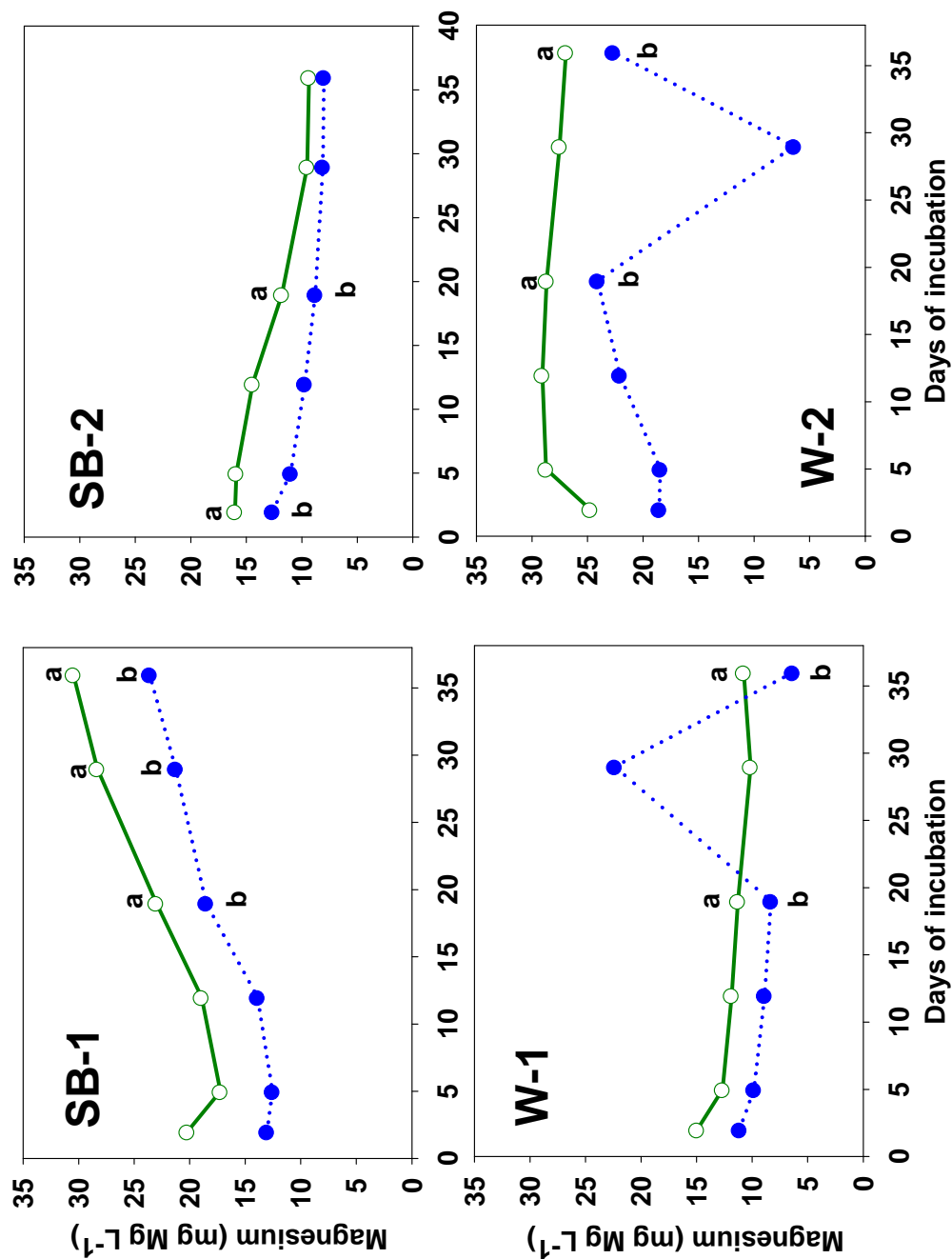


Figure 11. Floodwater dissolved calcium concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$

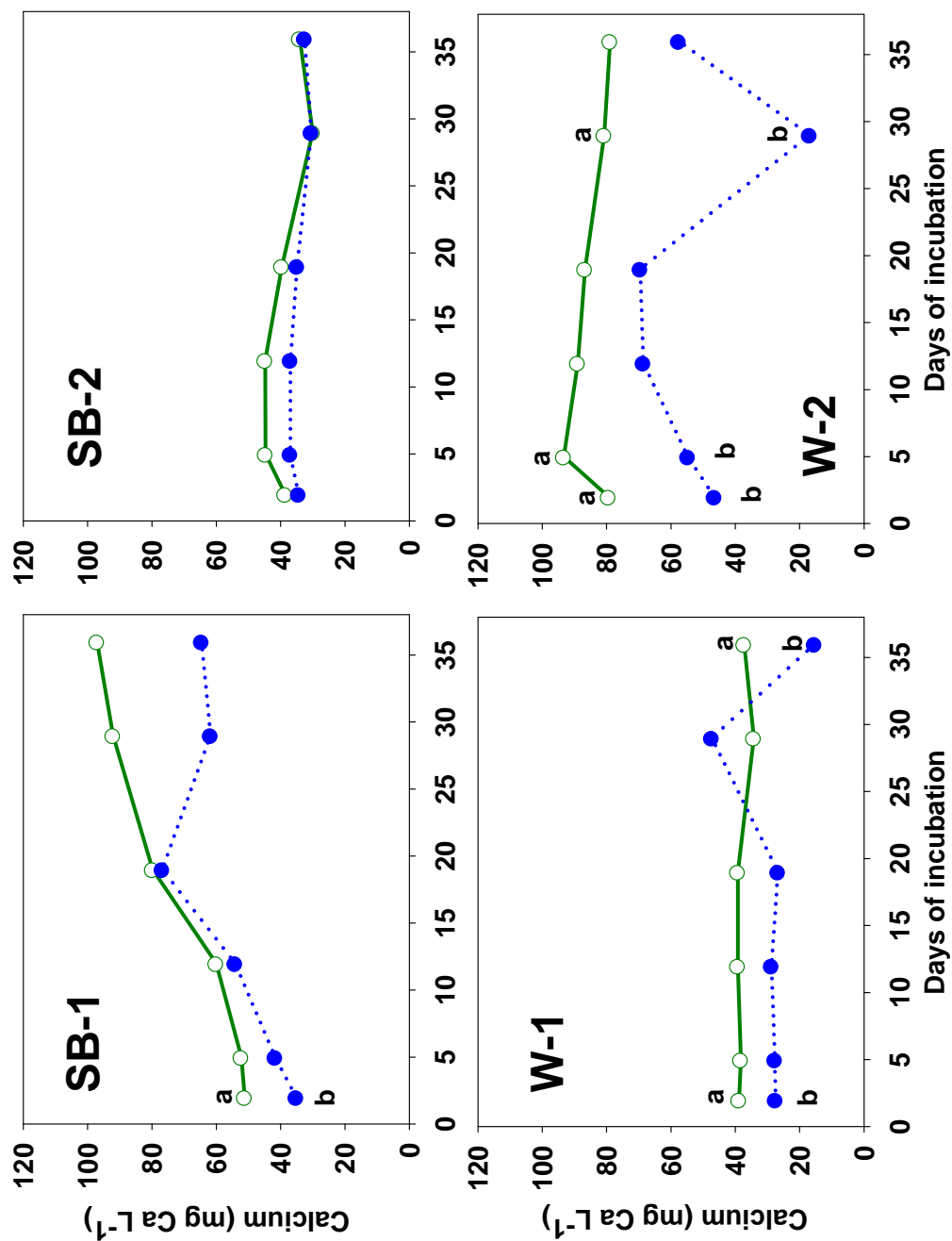


Figure 12. Floodwater dissolved sodium concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

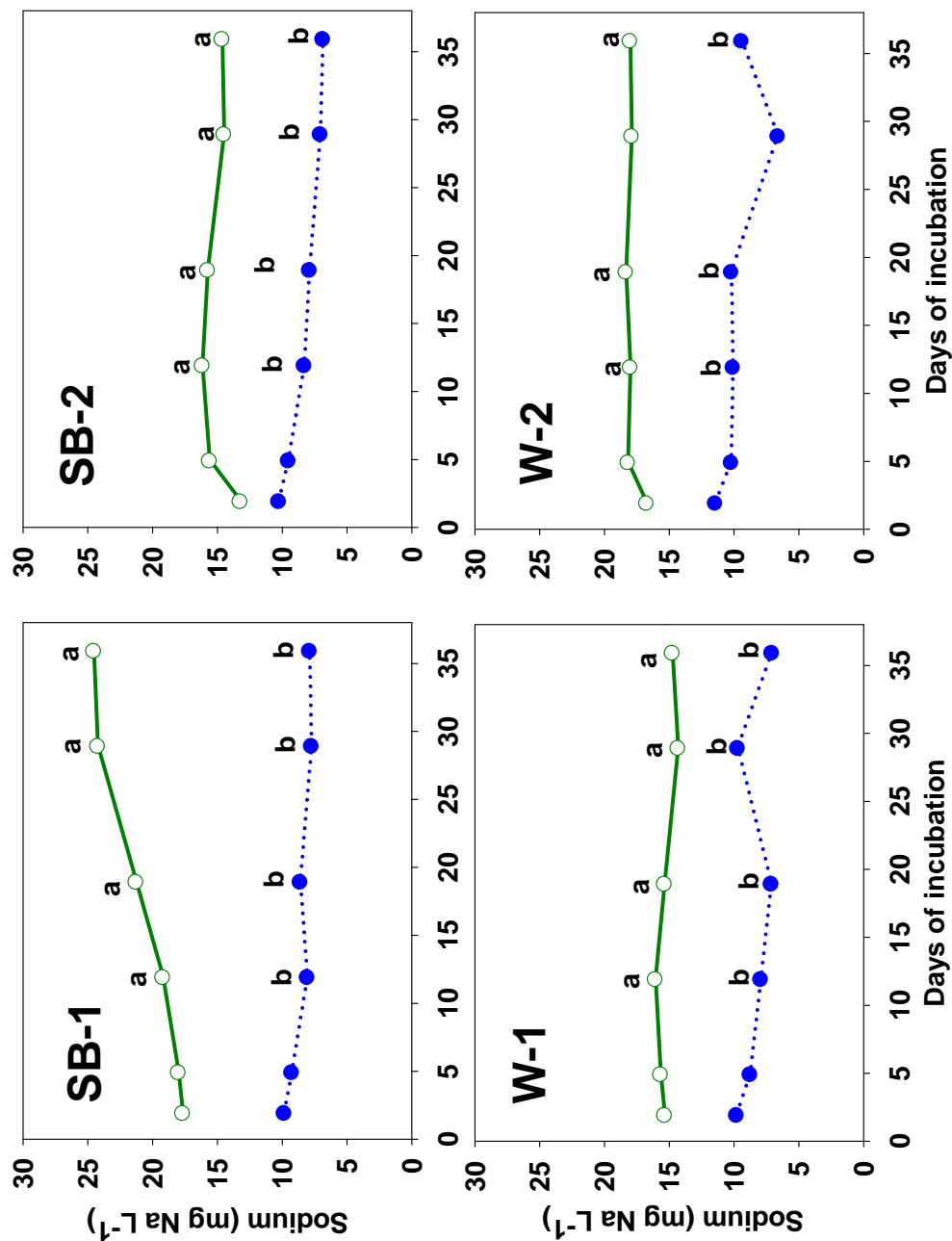
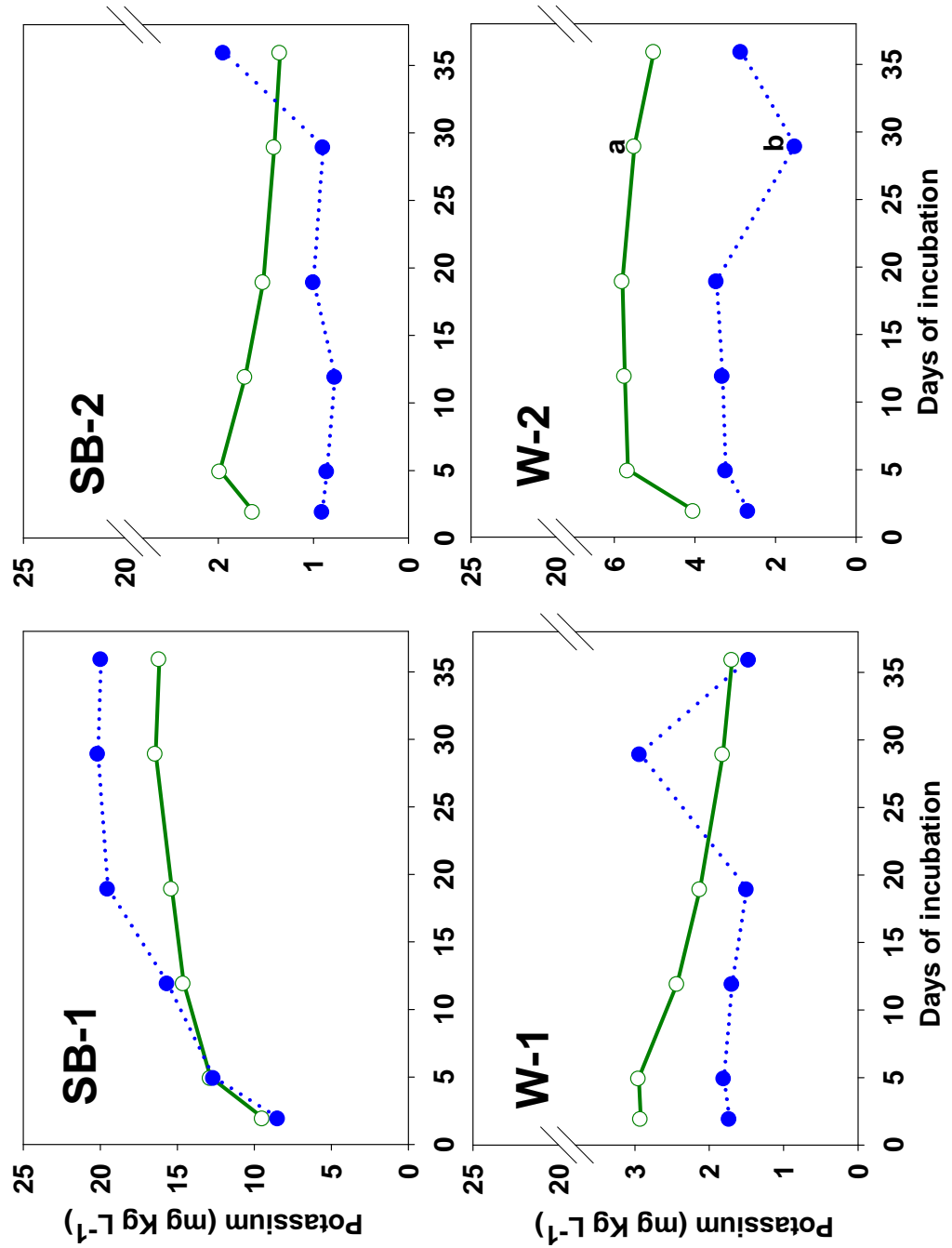


Figure 13. Floodwater dissolved potassium concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



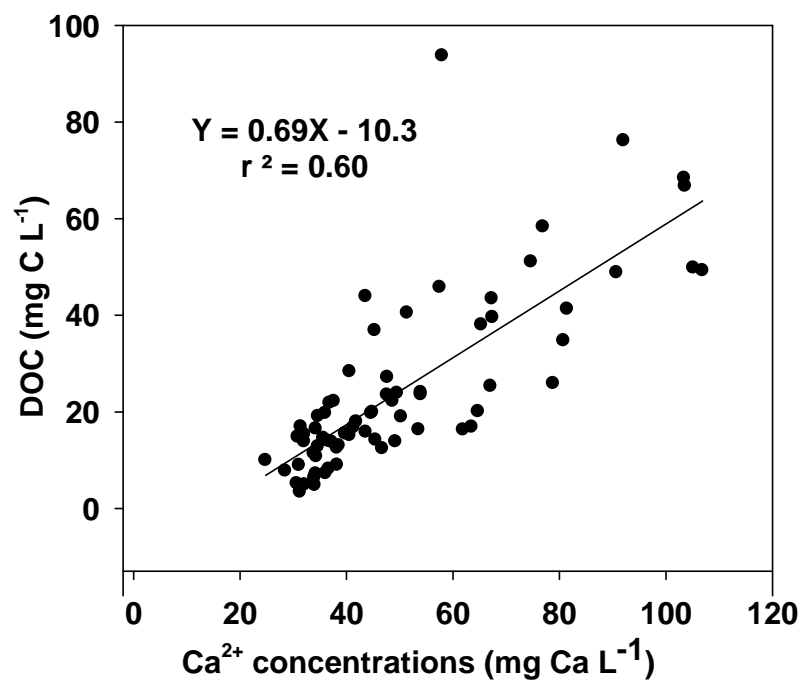


Figure 14. Statistical correlation between floodwater DOC and Ca^{2+} for the SB-1 and SB-2 cores. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.001.

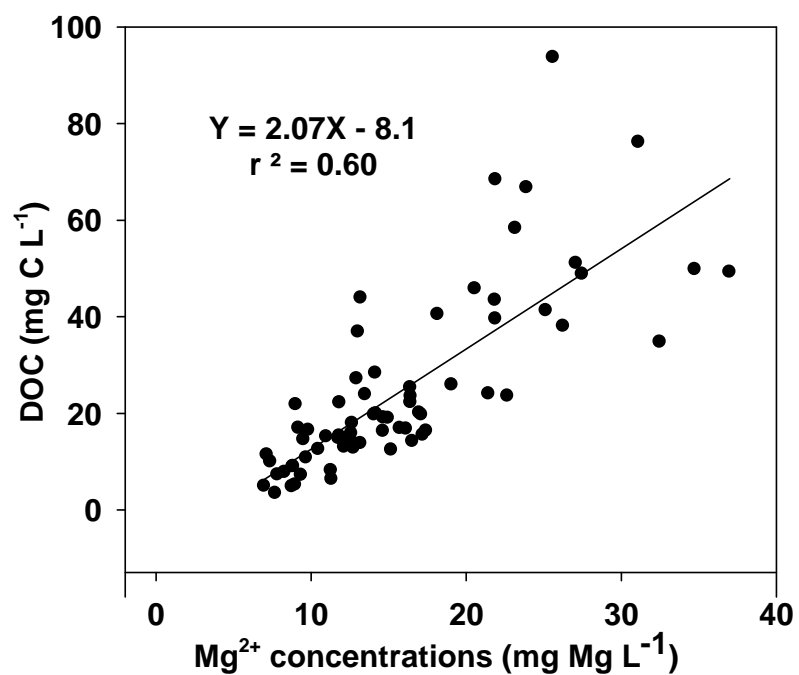


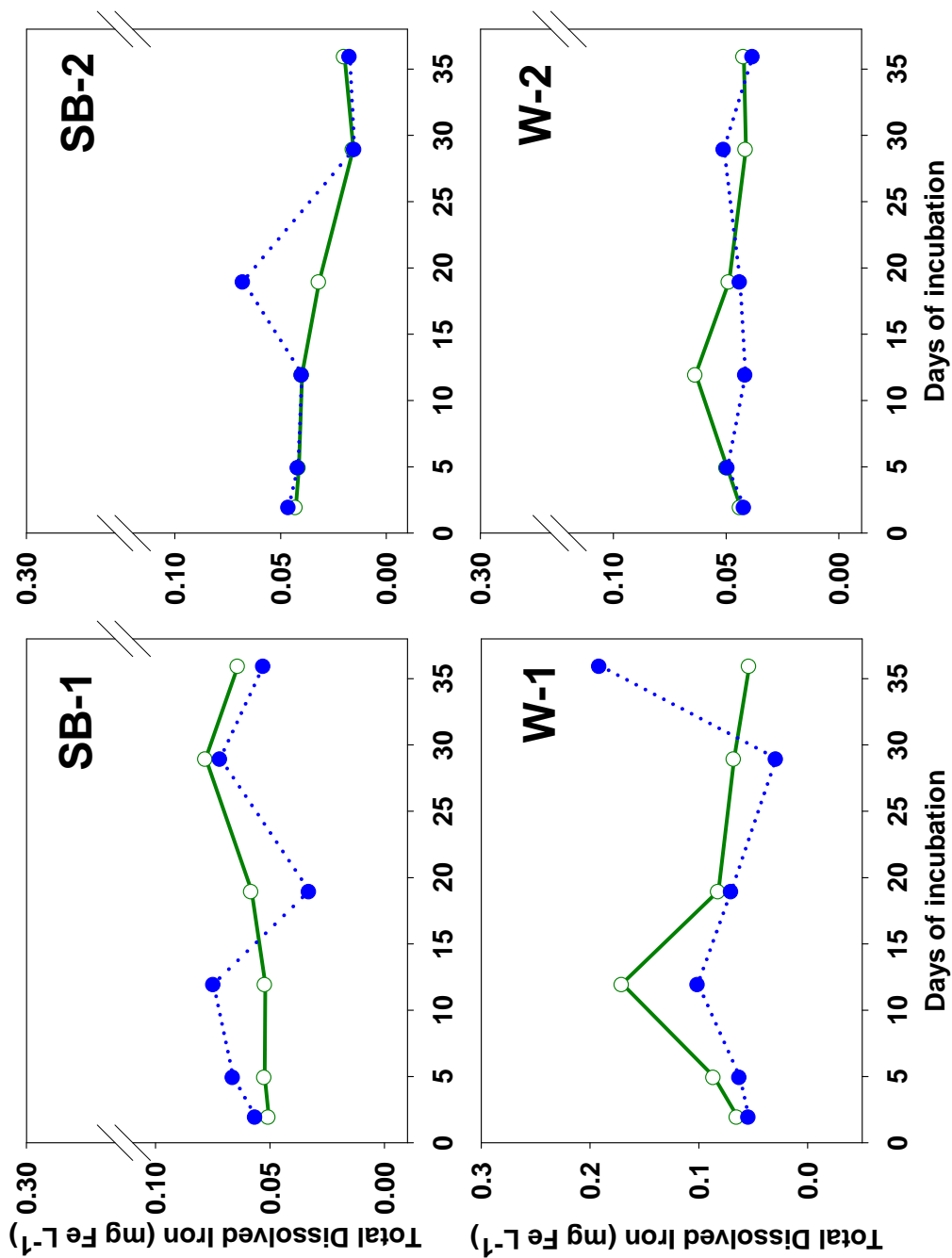
Figure 15. Statistical correlation between floodwater DOC and Mg⁺² for the SB-1 and SB-2 cores. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.001.

Dissolved Fe concentrations in sample water ranged between 0.015 and 0.19 mg L⁻¹ (Fig. 16). Overall, W-1 cores had significantly higher dissolved Fe concentrations compared to the other sites ($p > 0.05$), and there were no significant differences amongst treatments. Other than these few observations, there were no other significant links between the concentration of dissolved Fe and that of the other dissolved species considered in the study. Contrary to the study hypothesis, no trend was observed between SRP and Fe in the floodwater.

Due to some technical difficulties (clogged sampling ports), porewater was not extracted until Day 19 (sampling round 4). Porewater samples could be collected from about half of the cores; therefore, the data set remains incomplete and all discussion pertaining to porewater refers to roughly the second half of the experiment. However, after performing statistical correlations, the resulting data does show some interesting trends with regard to certain species. There were significant relationships among all cores with regards to the porewater samples between SRP and Mg²⁺ ($r^2 = 0.19$, $p < 0.05$) and SRP and Ca²⁺ ($r^2 = 0.27$, $p < 0.01$) (Figs. 17-18).

There were also interesting correlations between dissolved species in porewater and floodwater. There was a significant correlation between SRP concentrations in porewater and floodwater ($r^2=0.62$, $p<0.001$) (Fig. 19). From this correlation, approximately twice the amount of SRP was found in the floodwater compared to the porewater (Fig. 19). There were also significant positive correlations in porewater and floodwater with respect to Mg^{2+} and Ca^{2+} ($r^2= 0.47$, $p<0.001$ and $r^2= 0.45$, $p<0.001$, respectively) (Figs. 20-21). By interpreting these figures, Mg^{2+} was in equilibrium whereas Ca^{2+} was 1.5 times higher in the porewater compared to the floodwater (Figs. 20-21).

Figure 16. Floodwater dissolved iron concentrations. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



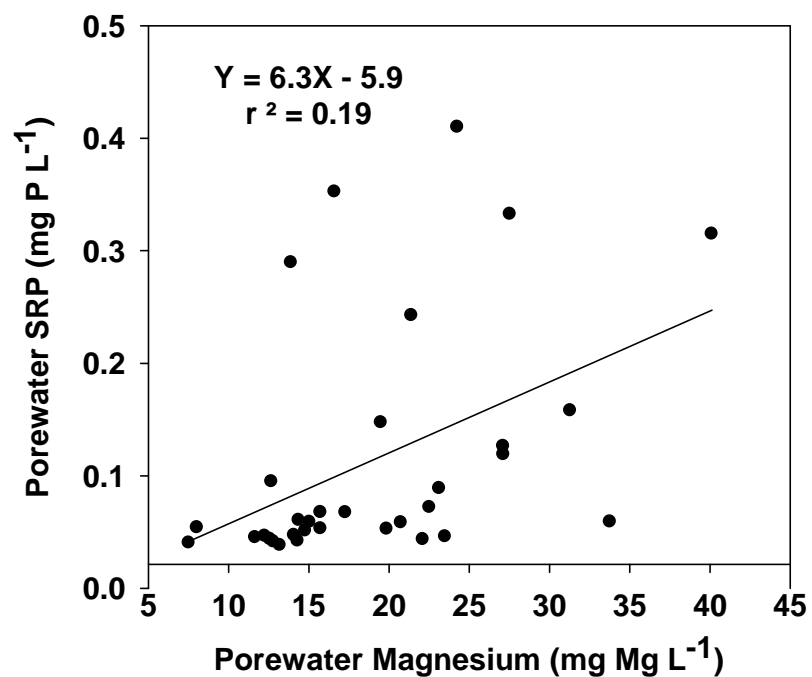


Figure 17. Statistical correlation between porewater SRP porewater and Mg²⁺. Graph displays data points from all sites for Days 19-36. No porewater samples were collected before Day 19. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.05.

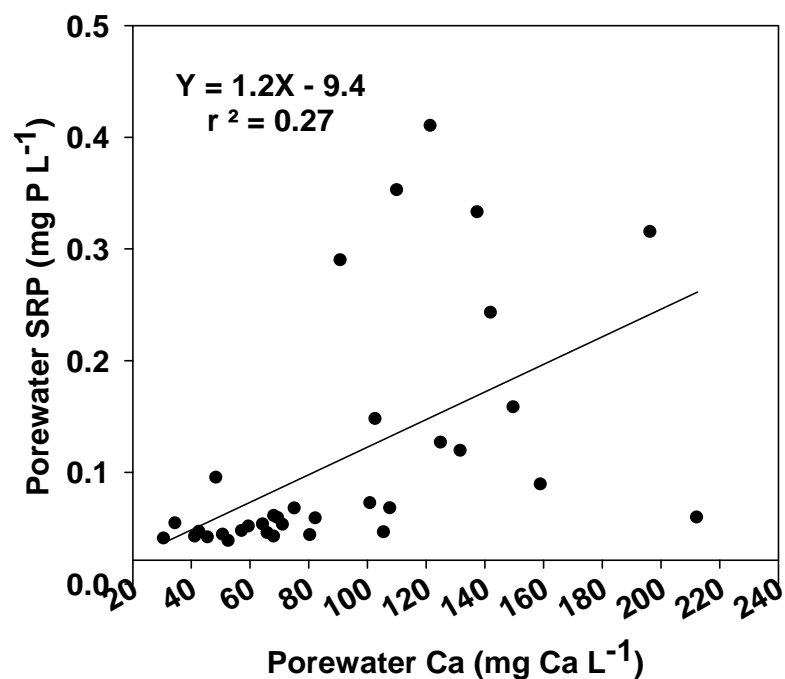


Figure 18. Statistical correlation between porewater SRP and porewater Ca²⁺. Graph displays data points from all sites for Days 19-36. No porewater samples were collected before Day 19. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.01.

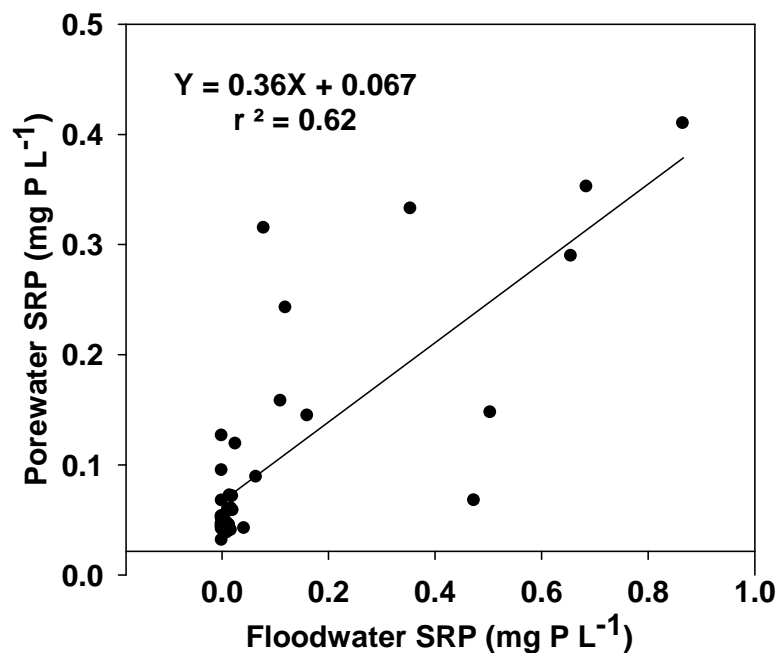


Figure 19. Statistical correlation between porewater and floodwater dissolved SRP. Graph displays data points from all sites for Days 19-36. No porewater samples were collected before Day 19. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.001 .

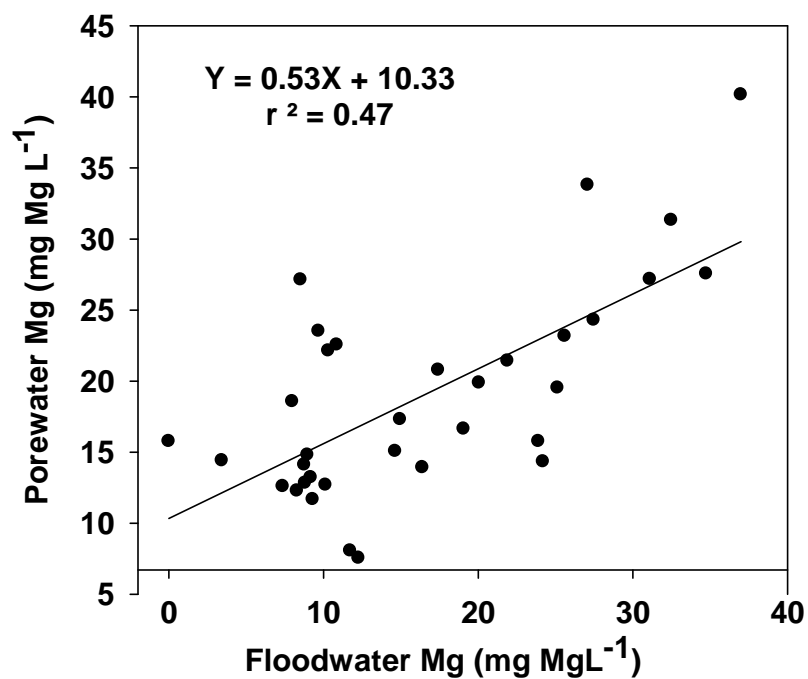


Figure 20. Statistical correlation between porewater and floodwater dissolved Mg²⁺. Graph displays data points from all sites for Days 19-36. No porewater samples were collected before Day 19. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.001.

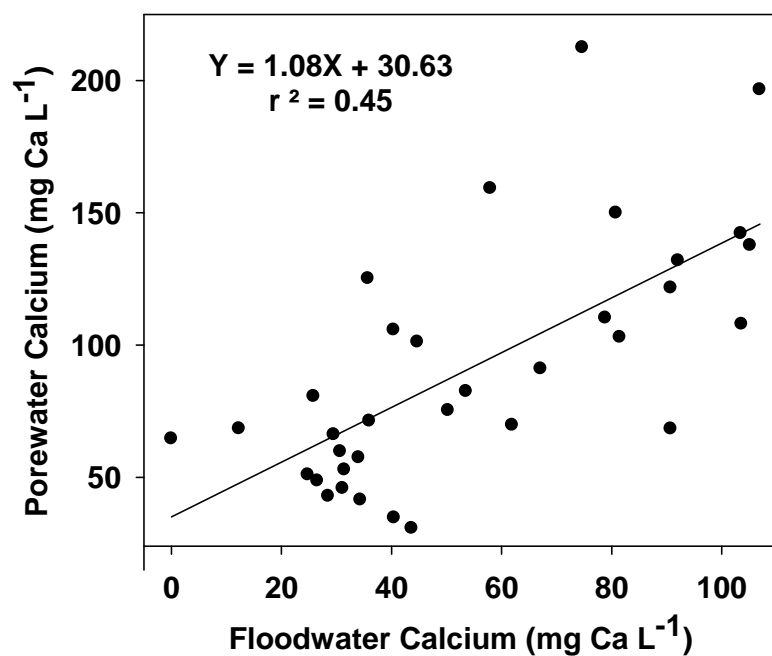
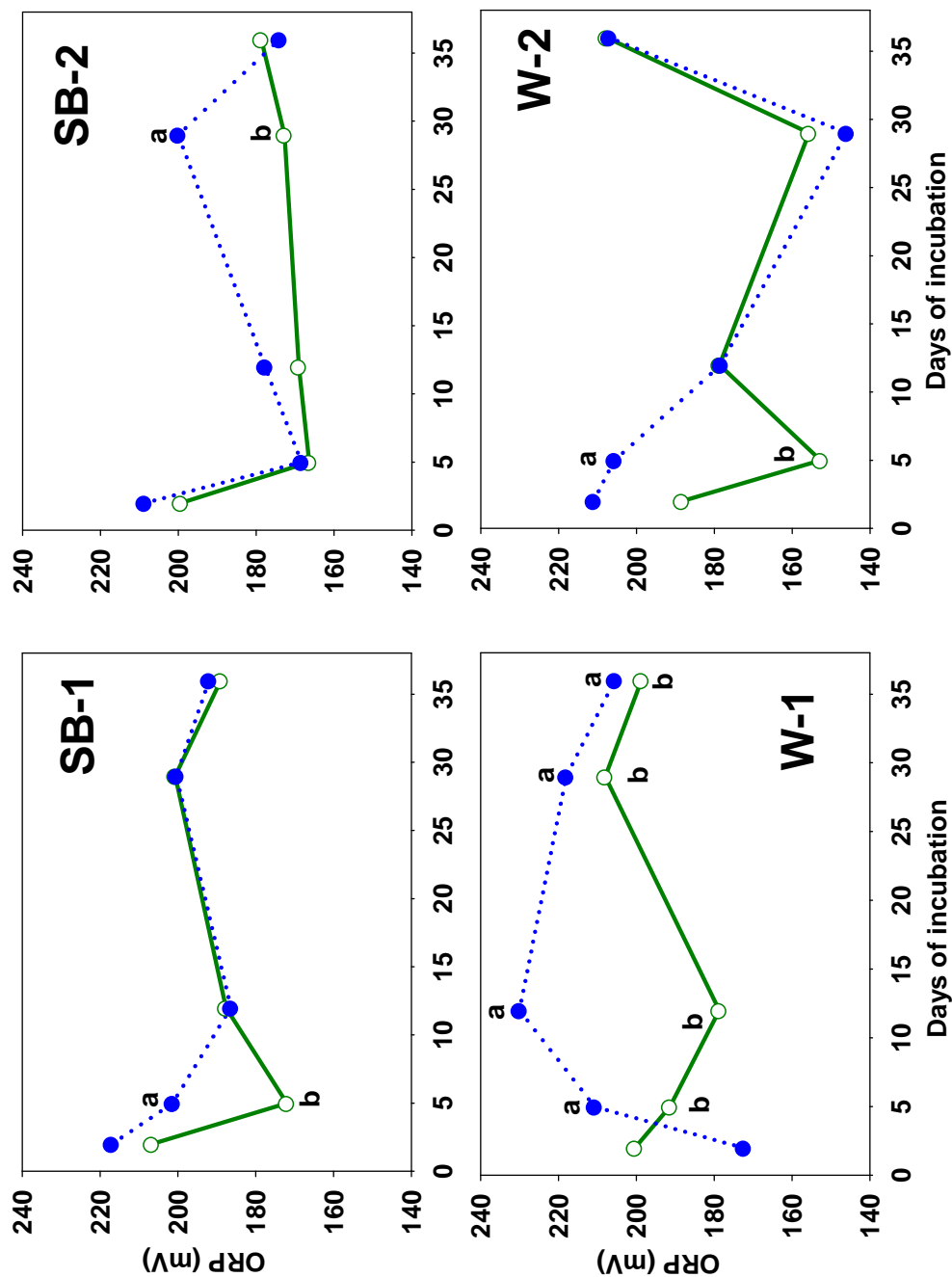


Figure 21. Statistical correlation between porewater and floodwater dissolved Ca⁺². Graph displays data points from all sites for Days 19-36. No porewater samples were collected before Day 19. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.001.

Electrochemical properties of the floodwater and porewater

Throughout the experiment, ORP in the floodwater ranged from 150-240 mV and therefore never became extremely anoxic. For the first 2 weeks, ORP decreased in all but the W-1 moist treatment cores (Fig. 22). After this initial drop, there was a small but steady increase in ORP until the end of the experiment (Fig. 22). No significant differences were found between treatments with regard to ORP in the floodwater. Despite some variability, porewater ORP steadily declined throughout the experiment, ranging from 32-183 mV on Day 19 to -54-111 on Day 36 (Table 10). Floodwater pH (6.8-8.7) was generally higher in the dry than in the moist treatment cores, but a significant effect of treatment was found only in the W-1 cores ($p < 0.05$) (Fig. 23). Throughout the experiment, pH in the floodwater steadily increased in both dry and moist treatment cores ($\Delta = 0.8$ pH unit). Porewater pH was not measured during the experiment.

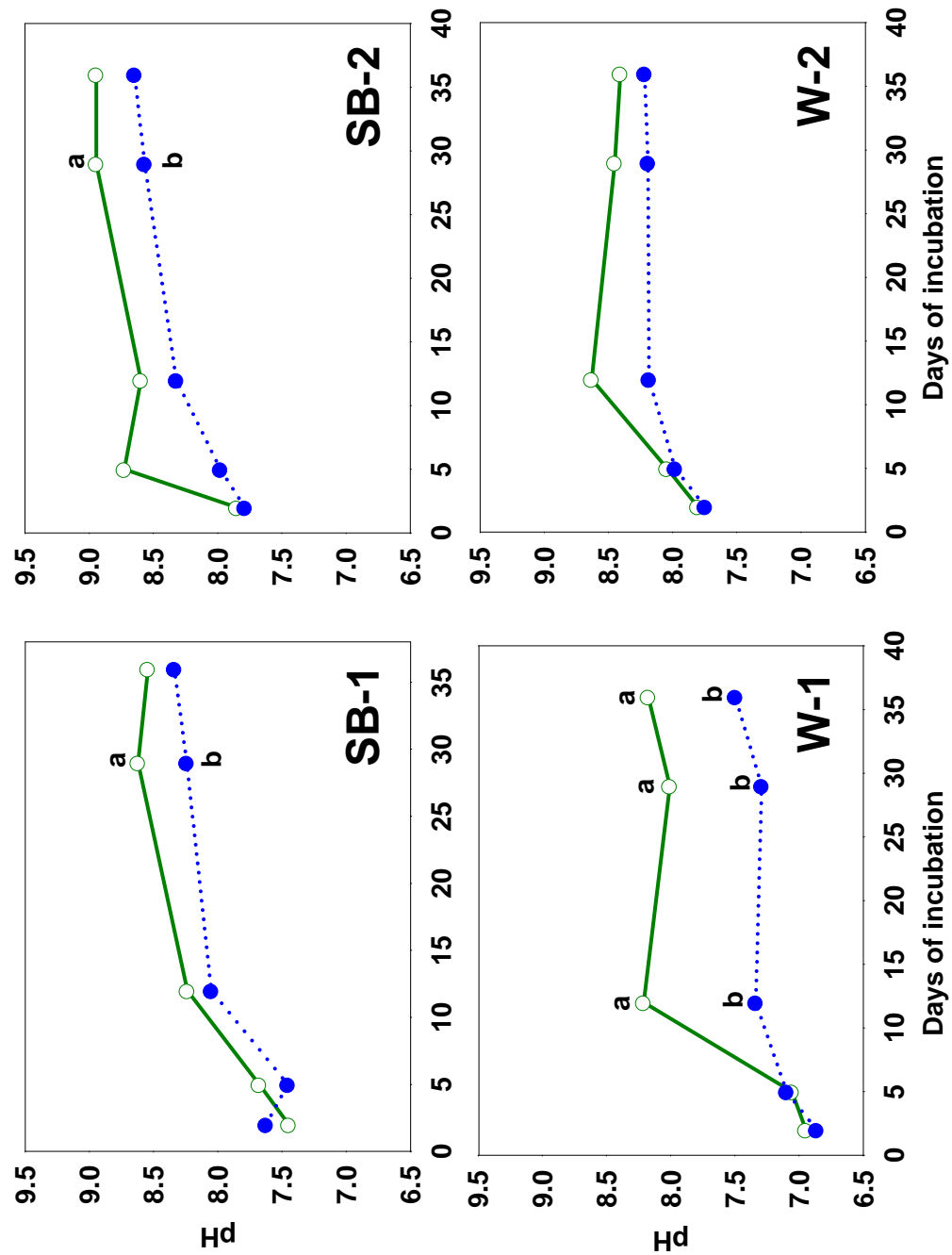
Figure 22. Floodwater oxidation reduction potential. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



Core name	Treatment	ORP (mV) Day 19	ORP (mV) Day 29	ORP (mV) Day 36
SB 1 - A	Dry	122	72	6
SB 1 - B	Dry	118	128	-1
SB 1 - C	Dry	72	-16	-32
SB 2 - A	Dry	51	104	ND
W 1 - A	Dry	ND	125	ND
W 1 - B	Dry	120	-85	-59
W 1 - C	Dry	-55	216	ND
SB 1 - B	Moist	128	-55	-98
SB 1 - C	Moist	148	-6	-10
SB 2 - A	Moist	150	38	120
SB 2 - C	Moist	155	164	103
W 1 - A	Moist	55	64	86
W 2 - B	Moist	183	181	ND

Table 10. Porewater ORP values for Day 19-36 sampling events. Porewater was extracted from sampling ports located approximately 10 cm below the surface of the soil. Large positive values indicate more oxidic conditions whereas values near or below 0 indicate more anoxic conditions. ND = Not determined.

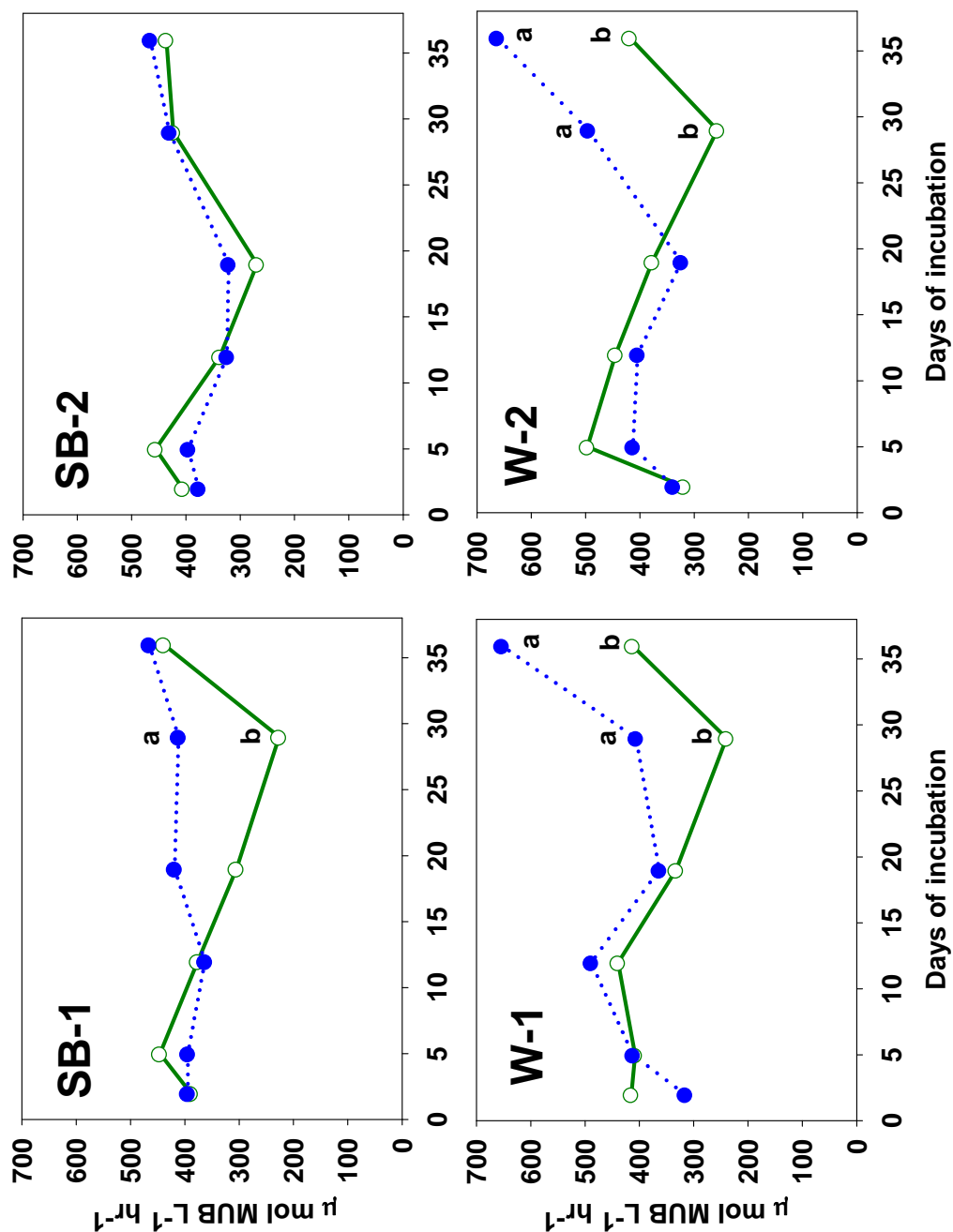
Figure 23. Floodwater pH. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



Acid phosphatase activity (APA)

In general, there was no significant effect of either treatment or site with respect to APA (Fig. 24). Aside from a small increase in activity in some cores (SB-1, SB-2, and W-2) during the first 20 days of the experiment, aqueous APA was very stable. There were no significant correlations between APA and the dissolved elements measured in the floodwater throughout the incubations.

Figure 24. Floodwater acid phosphatase activity (APA). Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.

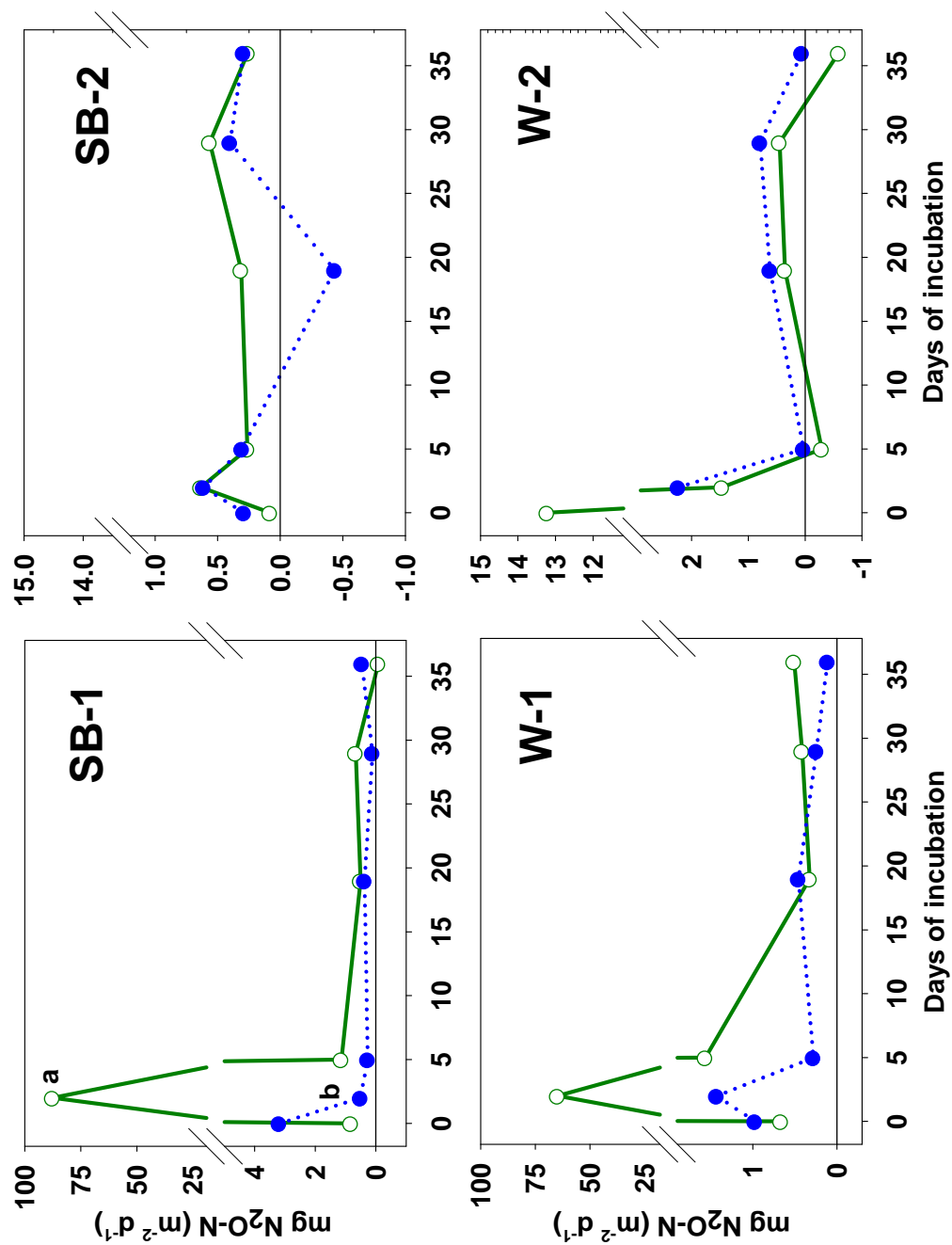


Greenhouse gas production

With the exception of SB-2 cores, the dry treatments resulted in significantly ($p < 0.05$) higher N_2O fluxes during the first week of the experiment (Fig. 25). These initial N_2O fluxes were particularly strong in the case of the dry SB-1 and W-1 cores. On Day 2, N_2O fluxes up to $87 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ were measured in the dry treatment. The maximum flux in the moist cores ($2.2 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$) was almost 40 times lower. In the SB-2 cores, no significant difference between treatments was noted. The initial burst in N_2O production was short-lived and was followed by a steep decline in emission rate by Day 5, dropping to around $0.5 \text{ mg N}_2\text{O-N m}^{-2} \text{ d}^{-1}$ for the remainder of the experiment (Fig. 25). This occurred in both treatments and in almost all cores and the trend was similar to that of NO_3^- . Consequently, a significant correlation ($r^2 = 0.78$, $p < 0.01$) was found between initial NO_3^- flux and N_2O emission during the first 2 weeks of the experiment (Fig. 26).

Carbon dioxide emissions were not significantly different amongst treatments throughout the duration of the experiment. In general, for the first 2 weeks of the experiment, the W-1 dry cores had the highest CO_2 fluxes while the SB-2 cores had the lowest (Fig. 27).

Figure 25. Core headspace nitrous oxide production. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



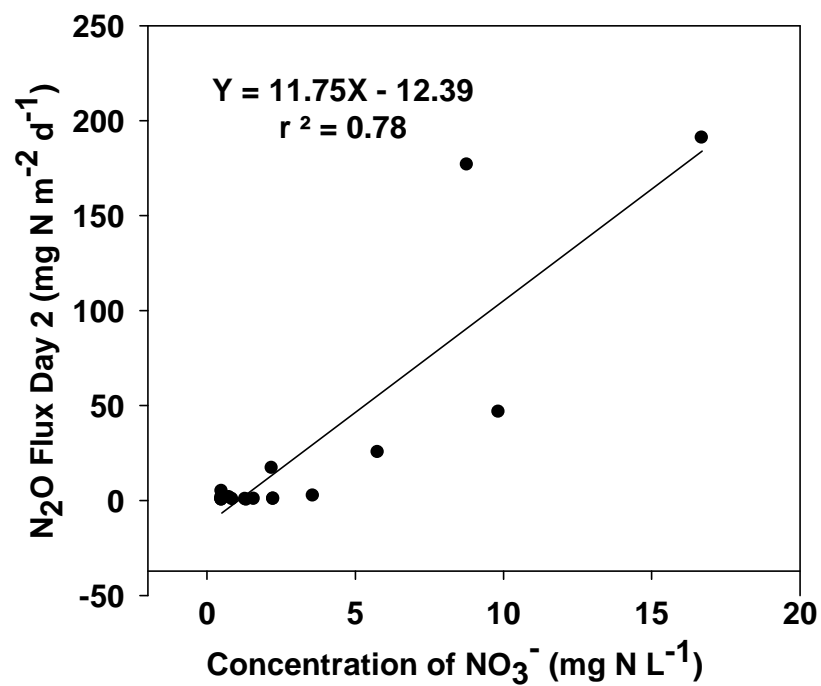
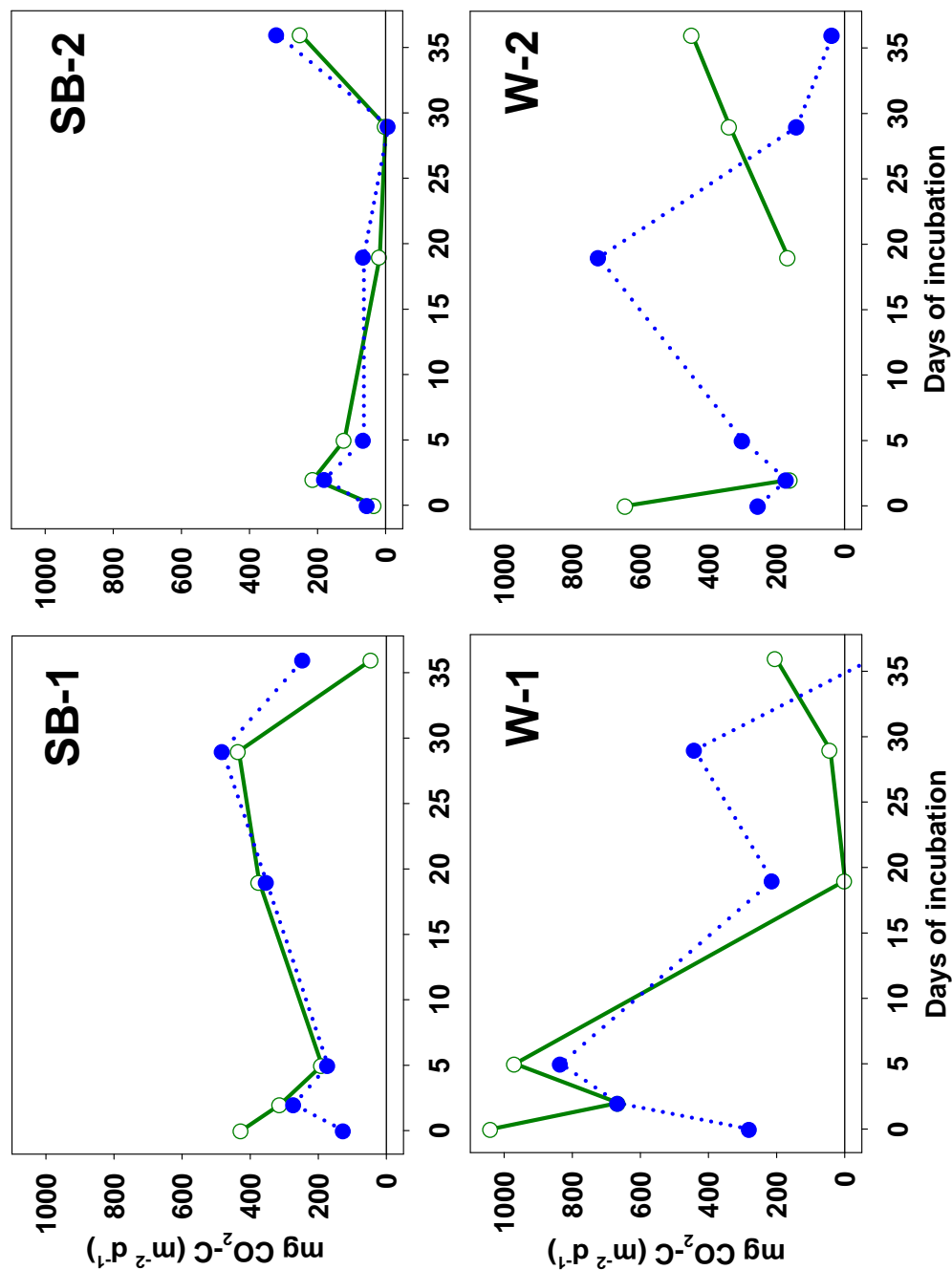


Figure 26. Statistical correlation between N_2O flux and NO_3^- concentrations. Graph displays data points from all sites for sampling Day 2 of the experiment. Equation of the line and corresponding r^2 value is shown on the graph. Correlation statistics results indicate a p value <0.01 .

Figure 27. Core headspace carbon dioxide production. Solid lines with hollow circles indicate dry treatments and dashed lines with filled circles indicate moist treatments. Data points on a given sampling date are labeled with different letters indicating a statistical difference at $p < 0.05$.



DISCUSSION

Nitrogen dynamics in current cropland and constructed wetland soils

The dry treatment results showed good evidence of N mineralization, as reflected by the positive flux of NO_3^- measured in the floodwater during the first days of the experiment. During the drying phase, organic matter mineralization may have occurred, resulting in the conversion of organic N into NH_4^+ via ammonification and then into NO_3^- by nitrification. These biochemical conversions were likely due to the oxidizing conditions created in soils during the drying phase (Kadlec and Wallace, 2009). A second trend that supports N mineralization in the dry cores was the increase in NH_4^+ concentration upon wetting. The release of NH_4^+ to the core water indicates that a portion of the organic matter pool underwent mineralization (ammonification) during the drying phase of the experiment (Mian et al., 2008).

Prolonged drying can cause organic matter mineralization as well as death of soil microbes. Coupled with dead soil microbes, organic matter turnover can also contribute to a flush of DOC after wetting (Mikha et al., 2005). Consistent with the study hypothesis, DOC increased after wetting in the dry cores. Microbial death and organic matter mineralization were probably not as significant in the moist treatment. Dissolved organic C availability combined with an increase in NO_3^- (Figs. 3 and 7) provided good conditions for denitrification as evidenced by the high rates of N_2O emission in the dry cores. The ORP results (ranging from 150-240 mV) also confirmed that conditions were favorable for NO_3^- consumption since denitrification can occur at or below redox potentials of 250 mV (Mitsch and Gosselink, 2007). The direct correlation ($r^2 = 0.78$, $p < 0.01$) between NO_3^- concentrations and N_2O flux (Fig. 26) as well as several published

studies support the interpretation that denitrification was an important N transformation pathway (Groffman et al., 1999). In addition, since N_2O fluxes dropped later in the experiment despite a constant level of DOC, these results suggest that denitrification was limited by the availability of NO_3^- and not by organic matter.

After wetting, the flux of NO_3^- in the dry treatment was short-lived in most of the cores. In addition to denitrification, microbial assimilation and immobilization of mineral N may also be contributing factors. Corstanje and Reddy (2004) reported stimulation of microbial activity and rapid consumption of available NO_3^- upon flooding of dried wetland soils. Mikha et al., (2005) also reported similar findings. Upon flooding, microbes assimilate some of the mineral N while the rest is left behind to accumulate in the floodwater (Gregorich et al., 1994). Thus, the NO_3^- flux measured in the study is likely an underestimate of total mineral N production. In flow-through wetland systems, high rates of mineral N release and its transfer to surface waters can pose an impact to water quality. This could be a serious concern if the denitrification capacity of the constructed wetland is not fully established. The SB-2 cores (sub-surface) results could help illustrate this thinking. Unlike the rapid decline observed with the other cores, the decline in NO_3^- concentrations in the SB-2 cores was very gradual throughout the experiment. Carbon dioxide fluxes in SB-2 cores were also lower (Fig. 27). These results suggest that the subsoil may not sustain high populations of denitrifiers compared to the other sites. In general, soil microbial activity tends to drop sharply below the 20 cm depth range (Raubuch and Beese, 2005).

Corstanje and Reddy (2004) reported NO_3^- fluxes rates in the range of 134 to 144 $\text{mg N m}^{-2} \text{ d}^{-1}$ for nutrient enriched peatland soils, and attributed these high rates to the

large amount of soil organic matter (48% TC) at their sites. Despite much lower C content at the SB-1 site (2.2% C, Table 2a) for example, it is informative to note that initial NO_3^- release was comparable ($130 \text{ mg N m}^{-2} \text{ d}^{-1}$) to the values reported by Corstanje and Reddy (2004), suggesting a much higher reactivity of cropland N compared to peatland N. Soil organic matter is made up of recalcitrant and easily decomposable compounds which can be quickly transformed by microbes into mineral forms. Since the highest NO_3^- fluxes were measured in the SB-1 cores, organic matter at this site probably contains more mineralizable N than at the other sites. Since the SB-1 cores were from an actively managed cropland, this interpretation is supported by the results of Boyer and Groffman (1996) who reported significantly higher pools of bioavailable N in cropland compared to forest sites in Northeastern US.

Total P and its relation to P release in constructed wetlands

Studies investigating the effect of wet/dry cycles on P release have been conducted with both TP-enriched and low TP soils. Past studies (Corstanje and Reddy, 2004; Bostic and White, 2006) have reported the release of significant amounts of P after drying and flooding of P “enriched” sites. Corstanje and Reddy (2004) measured P fluxes in peatland soils ($\text{TP} = 878 \text{ mg kg}^{-1}$) in South Florida, reporting fluxes averaging $48 \text{ mg P m}^{-2} \text{ d}^{-1}$ at these sites. The high organic matter content of peat soils (48% C) may have caused these very high P fluxes (Corstanje and Reddy, 2004; Bostic and White, 2006). In the present study, TP ($331\text{-}570 \text{ mg P kg}^{-1}$) was much lower than reported in Corstanje and Reddy (2004) so the lower amount of P released from these soils (0.09 to $2.9 \text{ mg P m}^{-2} \text{ d}^{-1}$) was to be expected. The SB-1 cores had the highest TP content and the

highest P flux, suggesting an agreement with the hypothesis that soils with high TP will release the most SRP upon flooding. However, it should be noted that soils with low TP have also been shown to release P upon flooding (Russel and Maltby, 1995). In the present study, for example, the SB-2 cores released appreciable amounts of P upon flooding even though the SB-2 soil had the lowest TP content. These results contradict several previous studies (Corstanje and Reddy, 2004; Bostic and White, 2006) and the above mentioned hypothesis. As alluded to in the N cycling discussion, OM quality (more than OM quantity) may better explain these results. The SB-1 and SB-2 soils may contain a relatively larger pool of mineralizable N and P compared to the other soils, allowing higher nutrient fluxes upon flooding. These results indicated that actively cultivated soils like those from the ST site, regardless of depth in the soil column, can release significant amounts of P after prolonged drying and subsequent flooding. Therefore, removing topsoil prior to wetland construction may not necessarily lead to less P export from newly constructed wetlands.

In addition to OM quality, the nature and strength of chemical associations between P and soil minerals could also contribute to the intensity of P release observed in the present study. As an alternative hypothesis, P associated with more soluble minerals may exist in the cropland soil, whereas these P pools may have already been depleted in the constructed wetlands after just a few years of operation.

The P fractionation results showed that the SB-1 cores had the highest water extractable P_i (WEP_i) and the highest P flux. These results demonstrate the ability of this P pool to pass into the aqueous phase. They also suggest that determination of this P

fraction could provide a relatively easy way to predict potential P export from recently created wetlands.

Contrary to the study hypothesis, SRP release was not correlated with porewater Fe or the amount of NaOH extractable soil P (Fe/Al bound P fraction). Based on several past studies (Aldous et al., 2005; Young and Ross, 2001), dissolution of Fe oxides under flooded conditions and SRP release (in porewater and floodwater) were expected. Throughout the experiment, however, no link was found between P release and dissolved Fe concentration. Further, the W-2 cores had the highest amount of Fe/Al-bound P (Fig. 2), but released minor amounts of P under both the dry and moist treatments. The duration of the flooding experiment (36 days) may have also contributed to the failure to detect reductive dissolution of Fe-bearing minerals. In order to release P bound to these minerals, redox levels need to be within the +100 to -100 mV range (Mitsch and Gosselink, 2007). Porewater ORP results (Table 10) indicate that reductive dissolution may have occurred in some, but not all of the cores. There is a possibility that Fe reduction could become an important mechanism of P release if the flooded mesocosms were monitored over a longer period of time (several months). However, Russel and Maltby (1995) also failed to find relationships between P release and dissolved Fe, even though conditions could have been conducive to Fe reduction. Surprisingly, the authors (Russel and Maltby, 1995) reported a decrease in P and ORP coinciding with an increase in Fe.

In contrast to dissolved Fe, positive linear correlations were found between porewater and floodwater with regards to SRP (Fig. 19), Mg^{2+} (Fig. 20), and Ca^{2+} (Fig. 21). While Ca^{2+} concentrations in the floodwater and porewater were in equilibrium (1:1

concentration ratio), Mg^{2+} concentrations were about 1.5-fold higher in the porewater than in the core water. The opposite was observed with regard to SRP concentration, being 1.5-2 times higher in the core water than in the porewater. Higher cation concentrations in porewater may indicate a transfer from the porewater to the core water. The spatial distribution of SRP would indicate that P was not being transferred from the porewater and that reductive processes were not a factor controlling P release. Although porewater was only collected during the second half of the experiment, this interpretation is still supported by the data because most of the P release occurred during the first 2 weeks of the study when strong reducing conditions had not yet developed. Based on these results, there is a possibility that Ca and Mg-bearing minerals may control P release in these Midwest soils. Future studies should examine these possibilities.

Effect of biomass production on nutrient concentrations

In addition to microbial uptake discussed in previous sections, unexpected growth of algae and macrophytes may have contributed to observed variations in core water composition. By the third week of the study, algae growth was visible in the moist treatment cores. Despite steps taken to remove biomass twice a week, algae and macrophyte growth could not be completely controlled as the experiment progressed. Algae were present in all cores while macrophytes were present in all but the SB-2 cores (possibly due to lack of seeds). These organisms may have provided another nutrient sink and could additionally explain the decline in SRP concentrations observed during the middle 2 weeks of the study. Algal biomass was not measured (not planned for in the study) but it was clear that the steady decline in SRP coincided with the emergence of

algae and macrophytes in the cores. The gradual increase in core water pH (Fig. 23) during the experiment may also be associated with algal growth (via CO₂ consumption). Therefore P uptake by algae could have influenced the outcome of the study and make interpretation of the results more challenging. However, the results discussed here reflect the possibility that, even in the real world, algae may influence the nutrient processing capacity of wetlands.

Impact of drying and wetting cycles on constructed wetlands in the Midwest

Since this study showed marked difference in nutrient release in current croplands versus established wetlands, this can help wetland managers predict startup nutrient releases in wetlands built upon mineral cropland soils of the US Midwest. As the moist treatment results have shown, allowing established wetlands to remain wet may reduce some nutrient release to receiving waters. However, keeping an entire wetland constantly flooded or moist may not always be possible due to evapotranspiration and lack of a consistent water source to replenish the wetland. Some constructed wetlands may also go completely dry between major rainfall events. Therefore, there is continuous threat of N and P release each time a wetland goes through cycles of drying and wetting.

This study also illustrates the need to understand nutrient release in soils at the surface and subsurface. Since wetland construction typically requires major soil disturbance, there may be loss of microbial functions due to topsoil removal. The results of this study show that there was much lower microbial activity in the subsurface cores although appreciable amounts of nutrients can be released from these cores. The loss of microbial function from topsoil removal is an important factor to consider regarding

nutrient retention in newly created wetlands. Conversely, there are disadvantages to constructing wetlands on the existing topsoil, such as the potential for nutrient enrichment (high antecedent P levels) and the presence of invasive seeds which can outcompete wetland plants.

Future Studies

From the results of this study, there are other potential studies that can be considered in order to gain a better understanding on the mechanisms of nutrient release in wetlands constructed in US Midwest agricultural landscapes. First, it would be interesting to find out if this mesocosm study results can be reproduced in the field. A post-storm sampling regime could be imposed at wetland sites following periods of brief and/or extended drought to capture the flux of N. These wetland sites could be of different ages to see if there is a difference between new and old wetlands with respect to nutrient release.

Due to the short duration of this study, there is the possibility that ORP did not become low enough to cause Fe reduction and subsequent release of P. A similar study could be performed for a longer period of time to determine if reductive dissolution occurs as ORP becomes more negative. The core volume of water used to flood the cores would have to be much larger in order to have enough water to sample a longer sampling period.

CONCLUSIONS

The results of this study help illustrate the mechanisms controlling nutrient release in response to drying and wetting cycles in wetlands developed on cropland soils of the US Midwest. Upon flooding, the dry treatment caused significant mineral N release at all sites probably due to organic matter mineralization. However, initial NO_3^- pulses were short-lived in most cases and were rapidly denitrified. The release of SRP could be significant in newly constructed wetlands affected by wet/dry conditions, and appears to be dependent on antecedent TP status and quality of organic matter. In comparison, P release from established wetlands could be minor. Although the magnitude was lower, P release was also important in cores containing soils from the subsurface. This was contrary to one of the study hypotheses that subsurface soils could act as a P sink upon flooding. Also contrary to the study hypothesis, P release was not dependent on redox conditions and was not correlated with dissolved Fe concentration. The results suggest that for US Midwest soils developed in calcareous glacial till, reductive dissolution may not be the controlling factor of P release. An alternative hypothesis is that, in these soils, SRP may be bound to Ca/Mg-containing minerals varying in solubility. Overall, this study shows that seasonal patterns in drying and wetting can cause significant P release in newly constructed wetlands whereas these alterations in hydrologic regimes can cause N release in both recent and established wetlands.

APPENDICES

Appendix A. Individual core floodwater data for Schoolbranch 0-20 cm (SB 1) and Schoolbranch 40-60 cm (SB 2) dry treatments. ND = not determined.

ICP and electrochemical results

Site name	Day of Incubation	Fe	Mg	K	Na	Ca	pH	ORP
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹		mV
SB 1 - A	2	0.05	21.44	10.88	18.01	54.00	7.33	213
	5	0.05	20.57	16.15	19.23	57.53	7.43	187
	12	0.05	21.86	19.60	21.85	67.31	7.84	209
	19	0.08	27.49	19.96	24.51	90.75	ND	ND
	28	0.12	34.75	21.26	27.99	105.18	8.53	211
	36	0.08	37.00	21.02	27.76	106.92	8.43	191
SB 1 - B	2	0.05	16.53	6.97	16.98	45.50	7.56	213
	5	0.06	12.94	8.84	17.28	47.68	7.64	159
	12	0.06	13.03	6.45	14.28	45.33	8.09	173
	19	0.05	16.40	8.01	16.97	67.09	ND	ND
	28	0.08	19.08	8.34	18.46	78.86	8.74	197
	36	0.05	21.90	9.05	20.01	103.47	8.69	188
SB 1 - C	2	0.05	22.67	10.52	18.00	53.97	7.45	194
	5	0.05	18.16	13.53	17.48	51.38	7.96	170
	12	0.05	21.89	17.72	21.45	67.44	8.78	181
	19	0.04	25.16	18.09	22.31	81.48	ND	ND
	28	0.04	31.12	19.62	26.19	92.09	8.59	194
	36	0.06	32.50	18.42	25.81	80.79	8.51	188
SB 2 - A	2	0.04	16.13	1.29	13.86	41.32	8.02	189
	5	0.04	16.42	1.38	16.67	48.68	8.30	165
	12	0.04	14.19	1.06	17.66	44.89	8.80	168
	19	0.03	9.19	0.87	16.35	31.44	ND	ND
	28	0.01	7.37	0.84	14.68	24.80	9.06	166
	36	0.02	7.69	0.81	15.37	31.31	8.90	167
SB 2 - B	2	0.04	14.67	2.03	12.12	34.70	7.68	205
	5	0.05	14.15	2.73	14.85	40.59	7.99	167
	12	0.04	12.65	2.49	15.53	41.86	8.62	170
	19	0.03	10.99	2.33	15.34	40.59	ND	ND
	28	0.02	9.36	2.21	14.72	34.26	8.80	176
	36	0.02	9.02	2.10	14.66	36.89	9.10	180
SB 2 - C	2	0.04	17.21	1.59	13.68	39.76	7.85	204
	5	0.04	17.12	1.83	15.29	44.69	9.89	167
	12	0.04	16.43	1.59	15.25	47.66	8.37	169
	19	0.03	15.17	1.38	15.51	46.75	ND	ND
	28	0.01	11.77	1.18	14.05	30.89	8.97	176
	36	0.02	11.33	1.14	13.83	34.02	8.83	189

Appendix A continued. Individual core floodwater data for Schoolbranch 0-20 cm (SB 1) and Schoolbranch 40-60 cm (SB 2) dry treatments.

Nutrient and enzyme results

Site name	Day of Incubation	NO ₃ ⁻	NH ₄ ⁺	DON	SRP	DOP	DOC	APA
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	μmol MUB mL ⁻¹ hr ⁻¹
SB 1 - A	2	16.71	0.87	2.59	0.82	-0.15	24.02	387.76
	5	2.68	1.02	5.70	0.56	0.41	45.76	479.13
	12	7.04	1.57	9.81	0.86	0.02	43.42	480.53
	19	0.27	0.09	2.57	0.87	0.11	48.82	330.31
	28	0.23	0.05	7.52	0.35	0.61	49.78	180.32
	36	0.25	0.06	3.23	0.08	0.25	49.25	403.78
SB 1 - B	2	5.76	0.66	5.73	0.81	-0.81	14.16	325.74
	5	1.06	0.09	2.49	0.41	0.89	27.17	467.78
	12	2.88	0.60	3.78	1.03	0.03	36.83	396.47
	19	0.27	0.06	1.35	0.66	0.25	25.29	256.28
	28	0.25	0.03	2.17	0.68	0.05	25.90	225.64
	36	3.45	0.04	0.71	0.12	0.49	68.36	518.00
SB 1 - C	2	9.84	0.65	7.75	0.88	-0.05	23.59	453.22
	5	0.23	0.04	2.52	0.76	0.00	40.49	390.72
	12	4.18	0.08	12.29	0.45	-0.05	39.54	252.11
	19	0.25	0.09	2.50	0.50	1.72	41.28	327.87
	28	0.24	0.06	21.51	0.03	2.61	76.15	273.74
	36	0.23	0.04	2.45	0.11	3.11	34.74	394.12
SB 2 - A	2	2.24	0.24	0.18	0.11	0.34	16.77	411.42
	5	5.27	0.04	4.25	0.01	0.17	22.21	456.27
	12	4.30	0.16	1.55	0.10	0.01	19.91	330.31
	19	2.97	0.05	3.40	0.01	0.13	16.93	284.34
	28	0.24	0.02	2.15	0.00	0.15	9.97	438.14
	36	0.24	0.02	0.57	0.00	0.70	3.45	455.01
SB 2 - B	2	1.59	0.33	1.69	0.31	0.10	19.08	352.51
	5	0.98	0.04	3.67	0.34	0.00	28.35	414.91
	12	1.47	0.19	3.45	0.43	-0.05	17.94	371.52
	19	0.24	0.02	3.45	0.35	0.01	15.15	275.49
	28	0.24	0.03	2.94	0.33	-0.01	7.18	428.58
	36	0.23	0.02	2.41	0.18	0.45	21.79	411.99
SB 2 - C	2	4.27	0.27	1.97	0.14	0.43	15.49	454.07
	5	5.16	0.04	2.12	0.16	0.05	19.72	495.97
	12	4.68	0.17	0.69	0.18	0.02	23.50	310.09
	19	3.00	0.04	2.55	0.07	0.08	12.40	247.69
	28	0.23	0.01	3.70	0.00	0.07	14.82	402.13
	36	0.23	0.02	2.13	0.00	0.09	6.35	440.47

Appendix B. Individual core floodwater data for Van Wert (W 1) and Whitley County (W2) dry treatments. ND = not determined.

ICP and electrochemical results

Site name	Day of Incubation	Fe	Mg	K	Na	Ca	pH	ORP
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹		mV
W1 - A	2	0.06	15.17	2.60	16.82	31.85	6.96	209
	5	0.07	12.80	2.90	18.26	30.72	7.05	187
	12	0.09	11.46	2.42	19.14	30.03	8.61	163
	19	0.07	10.70	2.10	17.77	29.24	ND	ND
	28	0.05	10.14	1.99	17.35	26.55	8.12	193
	36	0.06	10.35	1.78	17.18	26.94	8.52	199
W1 - B	2	0.07	12.12	3.08	13.77	40.78	6.92	229
	5	0.13	11.04	2.95	13.29	42.34	7.07	191
	12	0.25	11.08	2.81	13.97	44.42	8.15	169
	19	0.10	10.87	2.81	13.77	44.73	ND	ND
	28	0.04	8.54	2.12	11.52	35.72	7.94	215
	36	0.03	9.68	2.05	12.95	40.40	7.98	188
W1 - C	2	0.06	17.57	3.08	15.43	43.80	6.96	163
	5	0.06	14.15	2.99	15.40	41.75	7.05	196
	12	0.18	12.99	2.06	15.06	43.26	7.87	204
	19	0.08	12.27	1.46	14.52	43.66	ND	ND
	28	0.11	11.74	1.34	14.04	40.49	7.96	216
	36	0.06	12.22	1.25	14.08	44.34	8.02	209
W2 - A	2	0.04	26.75	3.81	15.18	78.76	7.78	188
	5	0.04	31.52	5.75	14.83	95.79	8.13	133
	12	0.07	31.11	5.57	14.22	69.65	8.79	173
	19	0.07	26.50	5.15	13.39	60.81	ND	ND
	28	0.02	24.17	4.53	12.24	52.59	8.67	184
	36	0.02	21.96	3.93	12.02	45.31	8.82	198
W2 - B	2	0.05	22.23	4.30	20.68	65.68	7.67	189
	5	0.06	24.13	5.53	24.15	79.44	8.02	162
	12	0.07	24.20	5.27	24.41	74.31	8.56	181
	19	0.04	24.82	5.56	25.52	77.53	ND	ND
	28	0.07	24.10	5.18	26.14	68.54	8.17	141
	36	0.06	23.16	4.63	25.94	71.40	8.15	209
W2 - C	2	0.04	25.29	3.99	14.38	93.66	7.96	188
	5	0.05	30.53	5.71	15.56	104.62	7.98	163
	12	0.05	31.89	6.36	15.35	122.93	8.54	182
	19	0.03	34.69	6.66	16.06	121.73	ND	ND
	28	0.03	34.23	6.78	15.24	121.12	8.51	142
	36	0.04	35.69	6.47	16.07	119.89	8.25	216

Appendix B continued. Individual core floodwater data for Van Wert (W 1) and Whitley County (W2) dry treatments.

Nutrient and enzyme results

Site name	Day of Incubation	NO ₃ ⁻	NH ₄ ⁺	DON	SRP	DOP	DOC	APA
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	μmol MUB mL ⁻¹ hr ⁻¹
W1 - A	2	2.19	0.70	2.17	0.08	0.23	20.69	381.15
	5	0.25	0.03	2.50	0.01	0.10	44.14	413.50
	12	0.62	0.55	2.08	0.02	0.10	39.59	495.05
	19	0.26	0.06	0.80	0.01	0.17	40.63	351.37
	28	0.23	0.02	8.26	0.00	0.11	40.75	243.23
	36	0.23	0.02	6.25	0.00	0.12	47.07	479.67
W1 - B	2	0.31	0.10	1.79	0.02	0.07	23.58	420.33
	5	0.35	0.03	3.53	0.01	0.07	40.07	401.62
	12	0.25	0.04	4.45	0.01	0.12	36.58	410.38
	19	0.24	0.05	7.46	0.02	0.07	34.58	295.69
	28	0.23	0.03	2.76	0.00	0.09	51.47	251.14
	36	0.50	0.02	4.91	0.00	0.17	101.17	387.10
W1 - C	2	8.78	0.91	-0.02	0.11	0.01	26.77	442.31
	5	0.23	0.04	4.18	0.02	0.18	61.35	408.02
	12	1.22	1.53	1.32	0.09	0.02	36.04	412.09
	19	0.24	0.04	4.56	0.02	0.16	49.48	349.87
	28	0.24	0.04	6.86	0.01	0.12	71.01	224.08
	36	0.24	0.04	15.56	0.01	0.14	129.78	370.53
W2 - A	2	1.85	0.60	1.97	0.04	0.12	19.52	358.52
	5	0.25	0.05	2.36	0.01	0.08	36.49	529.22
	12	0.48	0.33	1.41	0.01	0.09	37.60	364.90
	19	0.23	0.09	1.43	0.03	0.08	25.90	285.53
	28	0.24	0.03	7.73	0.00	0.08	29.69	293.61
	36	0.23	0.02	5.28	0.00	0.12	28.13	439.55
W2 - B	2	3.58	0.39	2.44	0.11	0.09	22.20	332.22
	5	0.25	0.03	2.83	0.03	0.07	41.32	580.81
	12	0.31	0.03	3.64	0.05	0.08	27.31	431.55
	19	0.25	0.08	1.13	0.07	0.03	39.43	461.08
	28	0.23	0.01	3.70	0.07	0.04	38.95	246.48
	36	0.26	0.02	2.53	0.02	0.34	42.87	419.50
W2 - C	2	1.30	0.08	1.91	0.04	0.11	16.98	267.75
	5	0.35	0.05	1.80	0.01	0.06	30.73	379.57
	12	0.23	0.04	2.35	0.01	0.11	20.91	537.15
	19	0.25	0.09	1.53	0.01	0.07	22.90	384.56
	28	0.23	0.03	3.97	0.00	0.08	34.88	231.56
	36	0.24	0.04	0.30	0.00	0.12	32.79	396.68

Appendix C. Individual core floodwater data for Schoolbranch 0-20 cm (SB 1) and Schoolbranch 40-60 cm (SB 2) moist treatments. ND = not determined.

ICP and electrochemical results

Site name	Day of Incubation	Fe	Mg	K	Na	Ca	pH	ORP
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹		mV
SB 1 - A	2	0.07	11.83	11.93	9.27	32.08	7.67	213
	5	0.06	11.84	18.54	8.94	37.65	7.61	202
	12	0.05	13.50	22.77	8.09	49.52	8.18	183
	19	1.78	16.99	25.18	7.52	64.75	ND	ND
	28	0.03	23.19	26.07	7.23	76.94	8.49	196
	36	0.04	26.26	25.41	7.20	65.34	8.40	195
SB 1 - B	2	0.05	14.07	12.03	10.25	36.05	7.48	216
	5	0.10	13.20	17.64	8.89	43.62	7.45	206
	12	0.50	15.73	22.43	7.75	63.57	7.87	192
	19	0.04	23.90	31.27	9.39	103.63	ND	ND
	28	0.15	25.61	32.38	8.45	58.00	7.99	204
	36	0.10	27.09	32.32	8.35	74.70	8.17	192
SB 1 - C	2	0.05	13.19	1.40	9.99	37.22	7.72	222
	5	0.04	12.60	1.70	9.88	43.64	7.30	196
	12	0.10	12.41	1.71	8.27	49.24	8.10	184
	19	0.03	14.64	2.04	8.84	61.92	ND	ND
	28	0.03	14.97	1.95	7.49	50.31	8.24	201
	36	0.02	17.44	2.09	8.08	53.56	8.44	189
SB 2 - A	2	0.05	12.50	0.93	9.62	32.07	7.88	199
	5	0.04	12.15	0.98	10.44	38.57	8.02	164
	12	0.04	10.47	0.90	8.73	38.24	8.34	171
	19	0.03	8.77	1.26	8.20	34.04	ND	ND
	28	0.01	8.97	1.00	7.71	30.70	8.73	190
	36	0.05	12.67	0.99	10.76	36.57	7.73	213
SB 2 - B	2	0.04	9.51	0.93	8.65	35.70	7.91	169
	5	0.04	8.86	0.83	8.20	38.29	8.50	175
	12	0.07	7.83	0.75	7.59	36.12	ND	ND
	19	0.02	6.99	0.82	6.64	32.13	8.58	192
	28	0.02	7.15	0.84	6.74	33.91	8.76	159
	36	0.05	12.74	0.80	10.35	34.65	7.75	214
SB 2 - C	2	0.04	11.29	0.67	9.45	36.68	8.00	172
	5	0.04	9.83	0.58	7.93	34.29	8.12	187
	12	0.10	9.69	0.98	7.86	34.35	ND	ND
	19	0.01	8.29	0.87	6.79	28.50	8.39	218
	28	0.02	8.82	3.05	6.94	31.12	8.53	189
	36	0.07	11.83	11.93	9.27	32.08	7.67	213

Appendix C continued. Individual core floodwater data for Schoolbranch 0-20 cm (SB 1) and Schoolbranch 40-60 cm (SB 2) moist treatments.

Nutrient and enzyme results

Site name	Day of Incubation	NO ₃ ⁻	NH ₄ ⁺	DON	SRP	DOP	DOC	APA
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	μmol MUB mL ⁻¹ hr ⁻¹
SB 1 - A	2	2.25	0.05	0.56	0.37	0.01	15.33	391.80
	5	0.23	0.08	2.40	0.48	-0.15	22.19	376.24
	12	0.97	0.11	3.88	0.44	-0.02	23.88	311.52
	19	0.23	0.05	0.15	0.57	0.27	20.07	468.61
	28	0.24	0.04	3.03	0.11	0.06	58.29	444.88
	36	0.23	0.02	5.99	0.03	0.12	38.01	566.54
SB 1 - B	2	0.28	0.15	0.94	0.39	0.02	19.69	448.68
	5	0.23	0.93	4.46	0.50	0.27	43.87	413.34
	12	0.23	0.40	5.75	1.00	0.43	16.89	441.83
	19	0.25	1.76	6.56	0.47	1.09	66.74	329.68
	28	0.27	0.13	11.86	0.06	0.04	93.71	408.55
	36	0.25	0.04	6.04	0.01	0.18	51.07	477.61
SB 1 - C	2	0.85	0.05	0.38	0.05	0.16	13.74	342.72
	5	0.39	0.07	0.62	0.03	0.09	15.81	393.20
	12	0.48	0.02	0.97	0.05	0.05	13.84	335.03
	19	0.23	0.04	0.49	0.02	0.08	16.30	457.29
	28	0.23	0.02	3.57	0.00	0.08	18.97	380.74
	36	0.24	0.02	1.48	0.02	0.07	16.33	352.40
SB 2 - A	2	0.44	0.09	0.72	0.05	0.14	13.83	388.47
	5	0.91	0.03	0.97	0.01	0.06	12.99	400.42
	12	0.76	0.01	0.36	0.02	0.08	12.54	326.73
	19	0.23	0.03	1.06	0.01	0.15	4.81	353.35
	28	0.24	0.02	2.71	0.00	0.19	5.14	447.37
	36	0.47	0.09	0.71	0.05	0.15	13.98	394.12
SB 2 - B	2	0.45	0.07	3.20	0.02	0.07	14.57	390.64
	5	0.68	0.02	5.93	0.04	0.05	9.01	267.19
	12	0.23	0.04	1.60	0.01	0.13	7.25	365.87
	19	0.23	0.03	5.89	0.00	0.09	4.89	387.65
	28	0.25	0.02	1.50	0.00	0.11	11.41	479.91
	36	0.42	0.06	0.59	0.05	0.16	12.81	347.25
SB 2 - C	2	0.81	0.04	1.17	0.01	0.07	8.15	394.74
	5	0.58	0.01	2.53	0.01	0.14	16.49	378.58
	12	0.27	0.02	1.29	0.01	0.08	10.76	244.24
	19	0.25	0.06	2.55	0.00	0.09	7.76	455.18
	28	0.24	0.04	1.61	0.00	0.18	8.97	389.28
	36	2.25	0.05	0.56	0.37	0.01	15.33	391.80

Appendix D. Individual core floodwater data for Van Wert (W1) and Whitley County (W2) moist treatments. ND = not determined.

ICP and electrochemical results

Site name	Day of Incubation	Fe	Mg	K	Na	Ca	pH	ORP
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹		mV
W1 - A	2	0.06	10.14	1.46	9.00	26.40	6.92	219
	5	0.07	8.79	1.62	8.07	25.26	7.01	213
	12	0.15	8.97	1.91	7.96	27.66	7.15	229
	19	0.05	9.32	1.41	6.95	29.50	ND	ND
	28	0.02	20.07	3.28	9.17	35.97	7.48	240
	36	0.04	10.32	1.43	6.61	25.84	7.47	210
W1 - B	2	0.04	13.58	1.92	10.96	32.39	6.77	129
	5	0.05	11.91	2.03	9.35	33.48	7.26	209
	12	0.05	9.72	2.08	8.46	35.81	7.49	229
	19	0.09	7.99	2.12	7.75	31.81	ND	ND
	28	0.03	24.65	1.49	9.78	67.54	7.03	ND
	36	0.35	2.81	2.12	8.89	10.78	ND	ND
W1 - C	2	0.06	9.68	1.81	9.40	23.67	6.90	169
	5	0.17	8.79	1.76	8.79	24.27	7.02	210
	12	0.28	7.90	1.08	7.31	22.74	7.37	232
	19	0.28	7.59	0.95	6.62	18.87	ND	ND
	28	0.04	22.35	4.03	10.17	38.41	7.36	196
	36	0.65	5.97	0.84	5.70	9.51	7.52	201
W2 - A	2	0.04	19.51	3.01	11.59	49.98	7.85	215
	5	0.04	19.21	3.54	10.52	61.21	8.18	206
	12	0.04	21.81	2.96	10.10	67.66	8.56	172
	19	0.04	22.75	3.24	10.08	57.53	ND	ND
	28	0.04	9.36	1.39	6.40	22.89	8.54	135
	36	0.03	19.43	2.97	8.55	40.39	8.57	201
W2 - B	2	0.04	16.18	2.09	10.61	46.92	7.69	213
	5	0.04	15.98	2.24	9.45	57.00	8.03	205
	12	0.04	22.49	2.26	10.44	85.67	8.22	178
	19	0.04	24.20	1.52	9.73	90.77	ND	ND
	28	0.06	3.44	2.36	7.65	12.31	8.18	150
	36	0.03	26.81	1.53	10.48	82.41	8.13	213
W2 - C	2	0.04	19.93	2.92	12.09	42.49	7.70	205
	5	0.07	20.12	3.91	10.66	45.92	7.73	206
	12	0.04	21.95	4.71	9.66	52.42	7.77	185
	19	0.05	25.30	5.60	10.76	60.21	ND	ND
	28	0.34	6.43	0.78	5.79	15.44	7.85	153
	36	0.06	21.83	4.06	9.21	49.92	7.95	207

Appendix D continued. Individual core floodwater data for Van Wert (W1) and Whitley County (W2) moist treatments.

Nutrient and enzyme results

Site name	Day of Incubation	NO ₃ ⁻	NH ₄ ⁺	DON	SRP	DOP	DOC	APA
		mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	μmol MUB mL ⁻¹ hr ⁻¹
W1 - A	2	0.23	0.10	0.57	0.03	0.10	17.72	296.36
	5	0.23	0.07	1.56	0.02	0.06	40.22	402.18
	12	0.23	0.03	2.64	0.01	0.08	24.44	466.32
	19	0.23	0.05	0.33	0.01	0.15	38.96	372.17
	28	0.23	0.09	3.05	0.00	0.11	17.52	414.72
	36	0.24	0.19	6.34	0.00	0.46	96.76	874.67
W1 - B	2	0.43	0.32	0.61	0.04	0.11	15.88	306.39
	5	0.26	0.19	2.04	0.01	0.04	29.53	426.29
	12	0.23	0.31	1.48	0.01	0.06	28.08	500.44
	19	0.25	0.04	2.25	0.02	0.08	26.14	351.99
	28	0.23	0.05	3.87	0.02	0.09	49.25	392.19
	36	0.28	0.06	17.42	0.16	0.59	77.72	612.73
W1 - C	2	0.76	0.50	0.47	0.04	0.12	16.44	343.25
	5	0.23	0.08	1.88	0.03	0.07	44.13	406.81
	12	0.26	0.10	6.77	0.03	0.19	17.97	498.52
	19	0.24	0.04	0.13	0.05	0.16	48.71	364.99
	28	1.26	1.49	18.71	0.01	0.34	36.47	410.64
	36	0.25	0.02	7.76	0.02	0.76	44.55	471.02
W2 - A	2	0.39	0.09	0.91	0.07	0.09	16.02	368.35
	5	0.23	0.05	0.44	0.01	0.05	18.96	417.34
	12	0.25	0.07	3.27	0.03	0.05	20.10	382.06
	19	0.25	0.04	3.33	0.01	0.13	17.75	240.66
	28	0.24	0.03	5.54	0.00	0.11	70.22	627.59
	36	0.25	0.03	5.31	0.03	0.12	20.25	869.32
W2 - B	2	1.34	0.05	0.61	0.15	0.44	14.28	297.82
	5	0.23	0.09	0.53	0.03	0.05	24.18	494.79
	12	0.23	0.07	6.21	0.07	0.04	20.25	382.46
	19	0.24	0.10	2.95	0.04	0.09	23.73	402.11
	28	0.29	0.24	6.96	0.02	0.15	60.46	444.26
	36	0.23	0.62	5.96	0.01	0.20	51.56	651.89
W2 - C	2	0.26	0.85	1.03	0.10	0.30	16.21	350.61
	5	0.42	3.12	6.74	0.01	0.06	19.94	325.85
	12	0.70	2.04	1.16	0.01	0.06	22.58	447.02
	19	0.40	4.11	7.40	0.01	0.11	23.08	329.05
	28	0.25	0.04	6.25	0.01	0.16	60.66	413.74
	36	0.89	0.30	9.22	0.01	0.11	71.42	467.29

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CURRICULUM VITAE

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Education

Indiana University Purdue University Indianapolis December 2010
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Teaching Experience

National Science Foundation GK-12 teaching fellowship
Center for Earth and Environmental Science, Indianapolis, IN June 2008 - May 2010

Professional Experience

Biogeochemistry Laboratory Technician
IUPUI Soil Biogeochemistry Lab, Indianapolis, IN July 2010 - September 2010

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Hydrologic Technician
Campbell Timberland Management, Fort Bragg, CA October 2005 - June 2008

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Watershed Steward's Project, Fort Bragg, CA October 2004 - August 2005

Service and Outreach Activities

Goose Pond Volunteer Biodiversity Assessment, Greene Co., IN, July 16, 2010

Pike Township Schools Science Night, Indianapolis, IN, March 4, 2010 and February 24, 2009

DSE Winter Teacher Workshop, Indianapolis, IN, February 27, 2010 and February 21, 2009

Hoosier Association of Science Teachers, Inc. (HASTI) annual meeting, Indianapolis, IN
February 3-5, 2010 and February 5-6, 2009

Earth Day Indiana 2009, Indianapolis, IN, April 25, 2009

Doe Creek Middle School Science Club, New Palestine, IN, March 12, 2009

Environmental Education Association of Indiana (EEAI) annual meeting, Camby, IN,
November 7-9, 2008

Fellowships and Awards

Division S-10: Wetland Soils Graduate Student Competition 2nd place poster presentation. Soil Science Society of America. December 2009

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2009 Recipient National Science Foundation GK-12 Graduate Fellowship

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Professional Affiliations

American Association of Agronomy - Crop Science Society of America – Soil Science Society of America (ASA – CSSA – SSSA), member

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Abstracts

Smith, A., Tedesco, L. P., and Furge, B., Soil Biology and Respiration. Annual GK-12 Meeting, March 26-28, 2010, Washington, DC

Smith, A., Jacinthe, P. A., Tedesco, L. P., Nutrient Cycling in Midwestern Agricultural Wetlands in Response to Altered Hydrologic Regimes. ASA-CSSA-SSSA Annual Meeting. November 1-4, 2009, Pittsburgh, PA

Smith, A., Cowan, A., Schilling, A., Tedesco, L. P., Furge, B., and Salazar, K., Discovering the Science of the Environment. Annual GK-12 Meeting, March 27-29, 2009, Washington, DC

Smith, A., Cowan, A., Schilling, A., Tedesco, L. P., Furge, B., and Salazar, K., Discovering the Science of the Environment. Midwest Regional GK-12 Meeting, November 7-8, 2008. West Lafayette, IN

Conferences Attended

National Science Foundation Annual GK-12 Meeting, March 26-28, 2010, Washington, DC.

Hoosier Association of Science Teachers, Inc., February 3-5, 2010, Indianapolis, IN.

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Environmental Education Association of Indiana (EEAI) Annual Meeting, November 14-16, 2008, Camby, IN.

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